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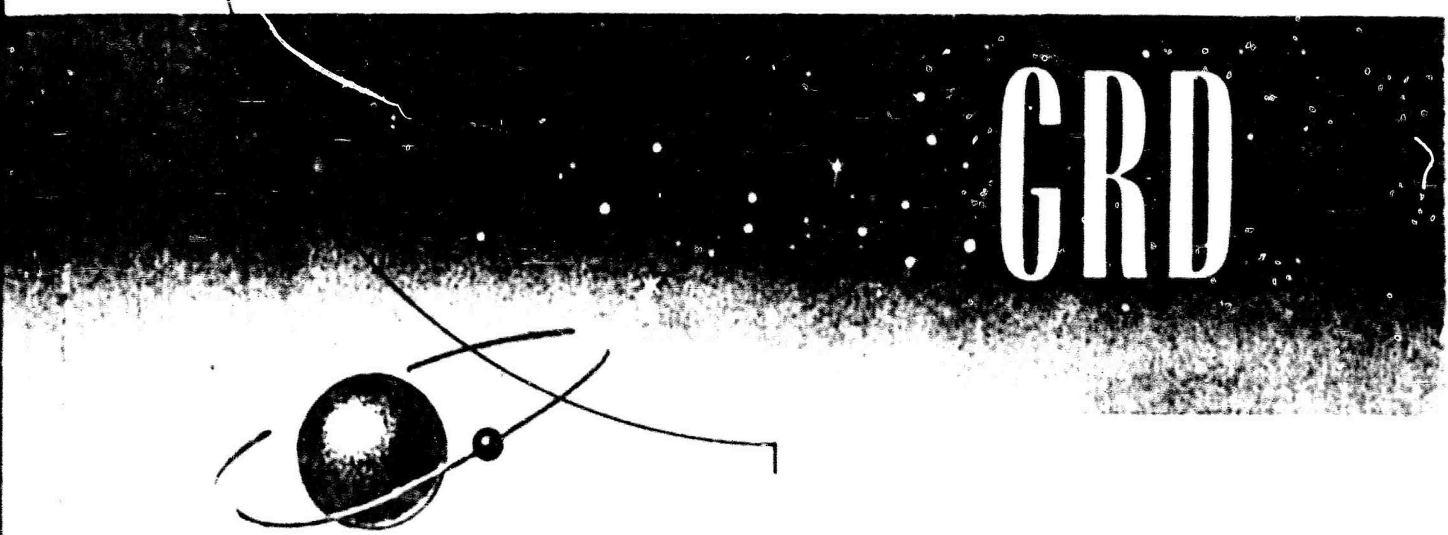
GEOPHYSICAL RESEARCH PAPERS

No. 71

THE CHEMISTRY AND VERTICAL DISTRIBUTION OF ATOMIC NITROGEN IN THE UPPER ATMOSPHERE

Lewis E. Miller

December 1960



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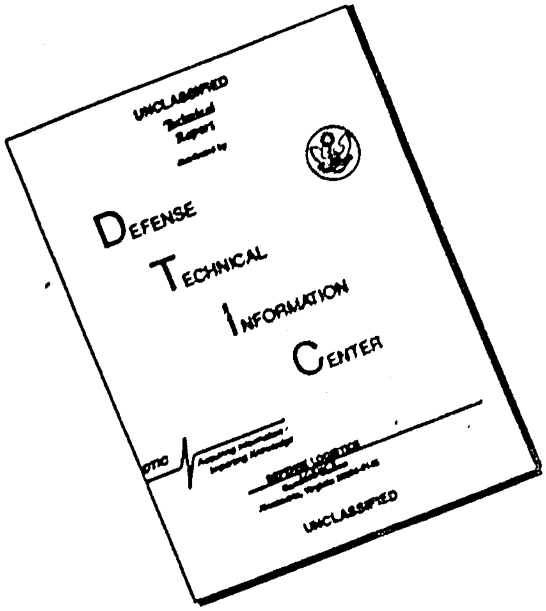

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Compiled under the sponsorship of the
Geophysics Research Directorate and the
National Aeronautics and Space Administration

Photochemistry Laboratory
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ACKNOWLEDGMENTS

The author's appreciation is extended to the Geophysics Research Directorate of the Air Force Cambridge Research Laboratories and to the Goddard Space Flight Center of the National Aeronautics and Space Administration for their cooperation in this study. Thanks are also expressed to Edith B. Meadows of the Planetary Atmospheres Branch of the Goddard Space Flight Center for her many helpful discussions and suggestions.

Special gratitude is due to Dr. Kenneth S. W. Champion of the Photochemistry Laboratory of the Geophysics Research Directorate who reviewed the manuscript, offered many valuable criticisms, and assisted in the manuscript revision.

FOREWORD

The prime objective of this literature search has been to summarize and appraise carefully and thoroughly the salient features of research papers which are applicable to the problem of atomic nitrogen in the upper atmosphere. The research papers which have been reviewed, some 540 in all, represent the most recent developments. These summaries, or abridgments, have been arranged chronologically by year and alphabetically within each year. They form the second part of this comprehensive examination of the literature. The first section is a summary and an evaluation of established knowledge that is currently available. This represents the author's views of the present status and the outlook for the future.

Evidence from the spectra of the auroral light and the night airglow indicates the presence of nitrogen atoms in the thermosphere. Theoretical considerations of solar radiation and its effect on producing photochemical reactions, photodissociation, photoionization, and recombination processes support the view that the yield of nitrogen atoms is possibly large in the F-regions of the ionosphere. There are many ramifications involved when considering the homogeneous gas reaction mechanisms that are possible in the formation of atomic nitrogen in the upper regions of the atmosphere and in its subsequent reactions with other atmospheric constituents.

The production of atomic nitrogen in the laboratory is intimately associated with the phenomenon of "active nitrogen". Extensive and thorough studies of the chemical nature of active nitrogen and its afterglow, especially those of Lord Rayleigh, supplied basic information which stimulated later investigations of the absorption and emission spectra of

molecular nitrogen and the correlation of the auroral spectrum in the upper atmosphere with that of active nitrogen.

More recently, solar corpuscular radiation as a heat source of the upper atmosphere has been considered to be due to the collision of solar particles with atoms and molecules of the dominant atmosphere components in which the vertical distribution of the constituent elements is significant. The production of atomic nitrogen in ionospheric regions by indirect mechanisms and reactions instead of direct dissociation as in the case of oxygen has now found general acceptance. The very great complexities of atmospheric processes which control phenomena in the upper atmosphere associated with the chemistry of nitrogen atoms motivated this study.

Lewis E. Miller

CONTENTS

Section | Page

FIGURES

SUMMARIZING TABLES

ABSTRACT

The topic, "The Chemistry and Vertical Distribution of Atomic Nitrogen in the Upper Atmosphere", may be regarded as a unit of a larger field, that of free radical chemistry. Atomic nitrogen like other free radicals is characterized as being electrically neutral and possessing an odd number of electrons. This latter characteristic accounts, in part, for its short lifetime and its highly reactive nature. An intensive and extensive review and analysis based on some 540 papers covering various aspects of the discovery of active nitrogen in the laboratory and the identification of atomic nitrogen in auroral and night airglow spectra have been summarized and given in tabular form. An integral part of the existence of atomic nitrogen in the upper atmosphere is the absorption of ultraviolet radiation by molecular nitrogen. Consequently such topics as absorption coefficients, dissociation energy of molecular nitrogen, discovery of the negative bands of N_2^+, and the various band systems of N_2 are included. More recently there has been an acute emphasis on the rates of free radical reactions and recombination coefficients. So far as is possible these data have been presented within the various summaries. The author and subject indices should aid in making this treatise a valuable and informative reference source.

THE CHEMISTRY AND VERTICAL DISTRIBUTION OF ATOMIC NITROGEN IN THE UPPER ATMOSPHERE

1. SUMMARY AND EVALUATION

1.1 INTRODUCTION

The advances made in exploration of the structure of the upper atmosphere with rockets and satellites to extreme altitudes have focused attention on the need for an accurate appraisal of the vertical distribution of the individual components in the earth's upper atmosphere. Composition of the atmosphere is an important parameter which enters into density, pressure, and temperature computation. A description of the geomorphology, or structure, of upper atmospheric conditions most often involves the temperature, T, as a parameter.

For example temperature is related to the ambient pressure as a function of height by the following form of the barometric equation

$$\frac{d \ln p}{dz} = - \frac{1}{H} = - \frac{Mg}{RT}$$

in which p, z, H, g, M, R, and T denote, respectively, the pressure, altitude, scale height, local acceleration of gravity, the mean molecular weight (or mean mole mass) of the atmosphere, the universal gas constant, and temperature in degrees Kelvin.

For all practical purposes the average chemical composition of dry air may be regarded as constant both in its geographical and its vertical distribution up to an altitude of about 100 kilometers. Above this altitude molecular oxygen (O_2) is dissociated by solar radiation.

(Author's manuscript approved 1 July 1960)

Here absorption in the Schumann-Runge absorption bands and its continuum (λ 1925-1300 A) produces atomic oxygen by the following process:

$$O_2 + h\nu \xrightarrow{\lambda < 1750\ A} O\ (^3P) + O(^1D)$$

As a result of this dissociation, the composition and consequently the molecular weight of the atmosphere varies with increasing altitude.

The status of nitrogen in the upper atmosphere is still uncertain. Photodissociation is much more difficult to achieve for molecular nitrogen than for molecular oxygen. Nitrogen is more readily ionized than dissociated, at least by solar radiation. Radiations shorter than λ 795 A are required to ionize molecular nitrogen while radiation at λ 2425 A can dissociate oxygen.

It is the purpose of this study to examine and evaluate the evidences in the literature for the occurrence, vertical distribution, and abundance of atmospheric atomic nitrogen. The forbidden lines of N I , λ 3466.4 A ($^2P - {}^4S$) and the doublet λ 5200 A ($^2D - {}^4S$) in the auroral spectrum give definite evidence of the presence of atomic nitrogen at least in the auroral region.

1.2 ISOTOPES OF NITROGEN

Ordinary nitrogen as it occurs in nature, both in the free state and the combined state, consists of two stable isotopes of mass numbers 14 and 15, $^{14}_{7}N$ and $^{15}_{7}N$, in the ratio 99.635:O.365. Four unstable radioactive isotopes $^{12}_{7}N$, $^{13}_{7}N$, $^{16}_{7}N$, and $^{17}_{7}N$ have been prepared.

1.3 PHYSICAL PROPERTIES OF NITROGEN

Briefly the solid, liquid, and gaseous states may be represented diagrammatically as follows:

$$N_2 \text{ (solid } \alpha\text{) cubic} \underset{}{\overset{35.66^{\circ}K}{\rightleftharpoons}} N_2 \text{ (solid } \beta\text{) hexagonal} \overset{63.19^{\circ}K}{\rightleftharpoons} N_2 \text{ (liquid)} \underset{(1\ atm)}{\overset{77.37^{\circ}K}{\rightleftharpoons}} N_2\text{(gas)}$$

$$\Delta H_{trans} = 54.71 \text{ cal mole}^{-1}$$

$$\Delta H_{fusion} = 172.3 \text{ cal mole}^{-1}$$

$$\Delta_{vaporization} = 1332.9 \text{ cal mole}^{-1}$$

TABLE 1. ISOTOPES OF NITROGEN[a]

Isotope	Type of Decay	Half-life	Mass Atomic
$^{12}_{7}N$	β^+, β^+ 3α	0.0125 s	12.0226
^{13}N	β^+	9.93 m	13.00991
^{14}N	99.635 percent abundance		14.00754
^{15}N	0.365 percent abundance		15.00489
^{16}N	β^-	7.35 s	16.0107
^{17}N	β^-, n	4.14 s	17.0139

(a) From J. M. Hollander, I. Perlman, and G. T. Seaborg, Rev. Mod. Phys., 25, 469-651, (1953).

The density of ordinary gaseous nitrogen at normal temperature and pressure is 1.25046×10^{-3} g cm^{-3}. This value corresponds to the molecular formula N_2. The normal state of the N_2 molecule is the triple-bonded state $X\ ^1\Sigma_g^+$.

TABLE 2. PHYSICAL PROPERTIES OF NITROGEN

Symbol	N
Molecular state of gas	N_2
Atomic number	7
Atomic weight observed	14.008
Atomic weight calculated	14.0073
Molecular weight	28.016
Melting point	$-210.0 \pm 0.1^{\circ}C$
Boiling point	$-195.8^{\circ}C$
Atomic volume	15.95 cm^3
Density	0.00125046 g cm^{-3}
Terrestrial abundance	46.3 g ton^{-1}
Ionization potential of molecule	15.6 ev
Ionization potential (atom) 1st	14.54 ev
Ionization potential (atom) 2nd	29.593 ev
Ionization potential (atom) 3rd	47.426 ev
Electronegativity (atom)	3.0 ev
Electron affinity (atom)	-0.72 ev
Crystal form	Cubic and hexagonal
Closest approach of atoms	1.42 A
Heat of fusion ($-210^{\circ}C$)	0.1732 kcal $mole^{-1}$
Heat of vaporation ($-196^{\circ}C$)	1.333 kcal $mole^{-1}$
Heat of dissociation $D_o(N_2)$	226 kcal $mole^{-1}$ or 9.764 ev
Free energy ($298.16^{\circ}K$)	31.654 cal $mole^{-1}$
Thermal conductivity cal. cm^{-2} cm^{-1} deg^{-1} sec^{-1}	0.600×10^{-4}
Atomic diameter in Kilo-X units	1.06

(or "crystal Angstroms" k X = A/1.0020)

TABLE 2. PHYSICAL PROPERTIES OF NITROGEN (Continued)

Spectral multiplicities	2, 4
Spectral term of normal state	$^4S^O_{3/2}$
Strongest spectral line A	λ 1134.98
K-limit ev	402.8
Electronic configuration	$1s^2\ 2s^2\ 2p^3$
*Atomic abundance (cosmic)	6.6×10^6 (Silicon - 1.0×10^6)

*From H. E. Suess and H. C. Urey, Rev. Mod. Phys., 28, 53, (1956).
For later estimates and discussions see:
(a) H.E. Suess, The Smithsonian Report for 1958, pp. 307-318, Smithsonian Institution, Washington, (1959);
and (b) A. G. W. Cameron, Astrophys. J., 129, 676-699, (1959).

References to Electron Affinity:

1. Lewis M. Branscomb, "Advances in Electronics and Electron Physics", Academic Press Inc., p. 49, New York, (1957).
2. H. R. Johnson and F. Rohrlich, "Negative Atomic Ions", J. Chem. Phys., 30, 1608, (1959).
3. Y. P. Varshni and S. N. Srivastava, "Electron Affinities of the Lighter Elements", Z. physik. Chem., (Leipzig), 206, 221, (1957).
4. Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond", Butterworths Scientific Publications, p. 40, (1950).

References to all other values:

Charlotte E. Moore, "Atomic Energy Levels", Circular 467, U. S. National Bureau of Standards.

William G. Meggers, "Key to the Welch Periodic Chart of the Atoms", 1959 Edition.

1.4 ELECTRONIC STRUCTURE

The nitrogen molecule has been extensively studied and more electronic states are known for it than for any other molecule. In its ground state it contains no unpaired electrons and has no resultant electronic angular momentum, either orbital or spin. Molecular nitrogen is diamagnetic with a susceptibility of -0.430 x 10^{-6} at 25°C. The molecular orbital electronic configuration for N_2 is represented by the notation KK $\sigma_{2s}^{2}\ \sigma_{2s}^{*2}\ \sigma_{2p_x}^{2}\ \pi_{2p_x}^{4}\ 2p_y$.

Studies of the vibrational and rotational spectra of molecular nitrogen reveal that there are two types of nitrogen molecules, those having symmetrical and those having antisymmetrical nuclear spins. The internuclear distance, based on spectroscopic data, in the normal electronic state of the gaseous N_2 molecule is 1.094 A [L. Pauling, The Nature of the Chemical Bond, 3rd ed., Cornell University Press, N. Y., p. 230, (1960)]. The inter-molecular forces are exceedingly small. The inert chemical behavior of molecular nitrogen has been attributed to the symmetry of the molecule and the stability of its electronic states. Pauling [Z. Naturforsch, 3a, 438, (1948)] has represented the electronic bond structure of the various excited states of diatomic nitrogen as symbolized in Table 3 in which r_e obs. is the observed equilibrium value of the internuclear distance, and A_o is the energy above the ground electronic state.

1.5 ACTIVE NITROGEN

Historically the knowledge of active nitrogen began with the investigations of Lewis in 1900. Lewis observed a peculiar fluorescent and afterglow effect when nitrogen was subjected to a strong condenser discharge, a spark gap, or a high frequency electrodeless discharge. Later, beginning in 1911 Strutt (later Lord Rayleigh) began an extensive

TABLE 3. ELECTRONIC STRUCTURE OF N_2

		r_e obs. A	A_o ev	Bond Structure
N_2	$X\ ^1\Sigma_g^+$	1.094	O	:N ≡ N:
	$A\ ^3\Sigma_u^+$	1.290	6.17	:N = Ṅ:
	$B\ ^3\Pi_g$	1.207	7.34	˙N ⩦ N:
	$a\ ^1\Pi_u$	1.207	8.53	.N ⩦ N:
	$C\ ^3\Pi_u$	1.144	11.01	·N ⩦ N:
N_2^+	$X\ ^2\Sigma_g^+$	1.113	O	·N ≡ N:
	$B\ ^2\Sigma_u^+$	0.071	3.18	·N ≡ N:

and comprehensive series of studies on the nature of active nitrogen: the chemical action of the afterglow of nitrogen on metals and nonmetals; the electrical properties of the afterglow; the kinetics of decay of the glow; the effect of impurities; and many other effects such as pressure, temperature, and energy. He attributed many of its properties to the presence of atomic nitrogen. In 1925 Sponer suggested that active nitrogen is atomic nitrogen and that the luminescence of the afterglow originates from the light emitted during the recombination of the nitrogen atoms.

During the ensuing years the similarity of the spectrum of the afterglow of active nitrogen to the auroral spectrum was noted. In a paper read before a meeting of the American Physical Society, 15-20 June 1931 at the California Institute of Technology, Kaplan announced that he had almost completely reproduced the auroral spectrum in the laboratory. The practical importance of such laboratory studies to the understanding of the night airglow and auroral phenomenon became recognized.

1.5.1 THEORIES OF ACTIVE NITROGEN

Many of the early workers studied the purity of nitrogen and the "wall effect" upon the nitrogen afterglow. As a result there developed much uncertainty and divergence of opinion on experimental details and interpretation of results. Briefly three entirely different theories have been suggested to account for the nature and properties of active nitrogen.

(a) CARIO AND KAPLAN'S THEORY

In 1929 Cario and Kaplan published a report on the investigation of the spectrum of the afterglow of active nitrogen. They attributed the bands of the first positive group in the visible afterglow to the emission from nitrogen molecules which are present in active nitrogen in the metastable state. The following mechanism involves a mixture of metastable atoms and molecules.

$$N(^2P) + N_2(A\ ^3\Sigma_u^+) \longrightarrow N_2(B^3\Pi_g) + N(^4S)$$

$$N_2(B^3\Pi_g) \longrightarrow N_2(A\ ^3\Sigma_u^+) + h\nu$$

(b) MITRA'S THEORY

Mitra ["Active Nitrogen - a New Theory", Assoc. Cultivation of Sci., Calcutta, India, (1945)] has considered that active

nitrogen consists of both nitrogen molecule ions in the $N_2^+(X')$ state and electrons. The following reaction was proposed:

$$N_2^+(X^1) + e^- + N_2 \longrightarrow N_2(B\ ^3\Pi_g) + N_2(A\ ^3\Sigma_u^+)$$

$$N_2(B\ ^3\Pi_g) \longrightarrow N_2(A\ ^3\Sigma_u^+) + h\nu$$

(c) THE ATOMIC THEORY

Lord Rayleigh from his numerous experiments on active nitrogen concluded that it contained nitrogen atoms. Later in 1925 Sponer suggested the same hypothesis and explained the afterglow as a three-body collision mechanism occurring in two stages.

$$N + N + M \longrightarrow M + N_2^{**} \longrightarrow N_2^{*} + h\nu \text{ (afterglow)} + M$$

During the past few years research on active nitrogen has been intensified, partly through the extensive investigations on free radical chemistry by Broida and his co-workers at the National Bureau of Standards, Washington, D. C. These researches have demonstrated that it is possible to trap and transport presumably atomic nitrogen collected in a matrix of molecular nitrogen at liquid helium temperature, 4.2°K.

Other later and important studies on the afterglow of active nitrogen have been made by Tanaka and co-workers at the Geophysics Research Directorate of the Air Force Cambridge Research Center; Oldenberg, Kistiakowsky, and others of Harvard University; Fontana of the U. S. National Bureau of Standards; Stewart and Emeleus of Queen's University of Belfast; Winkler, Schiff, and co-workers of McGill University, Montreal, Quebec.

The utility of these investigations on active nitrogen and its application to the upper atmosphere is evidenced by the fact that during the past decade these researches have received active financial support from various Government agencies. These include: the Air Force Cambridge Research Center; the U. S. Naval Research Laboratory; the Office of Naval Research; the United States Signal Corps; the National Defence Research Board, Ottawa, Canada; the U. S. National Bureau of Standards; Norwegian Research Council of Science and Humanities; the Gassiot Committee of the Royal Society, London; Air Research and Development Command.

These recent researches have elucidated the interactions which afford an explanation for the main features of the nitrogen afterglow. Referring to the electronic structure of the ground state ^4S nitrogen atom, $1s^2\ 2s^2\ 2p_x\ 2p_y\ 2p_z$, the three electrons in the 2p orbital have parallel (or unpaired) spins. Two nitrogen atoms may thus approach each other and interact along four different potential-energy paths, depending on the pairing of 6, 4, 2, and 0 electrons. The spectroscopic notation of these four paths are denoted by $^1\Sigma_g^+$, $^3\Sigma_u^+$, $^5\Sigma_u^+$, and $^7\Sigma_u^+$, respectively; Figure 1 illustrates these potential-energy paths.

Experimental evidence suggests the following transitions for the first stage (straw-yellow) of the Lewis-Rayleigh nitrogen afterglow.

$$N_2\ (B\ ^3\Pi_g) \longrightarrow N_2\ (A\ ^3\Sigma_u^+)$$

$$N_2\ (a\ ^1\Pi_g) \longrightarrow N_2\ (X\ ^1\Sigma_g^+)$$

$$N_2\ (\ ^5\Sigma_g^+) \longrightarrow N_2\ (A\ ^3\Sigma_u^+)$$

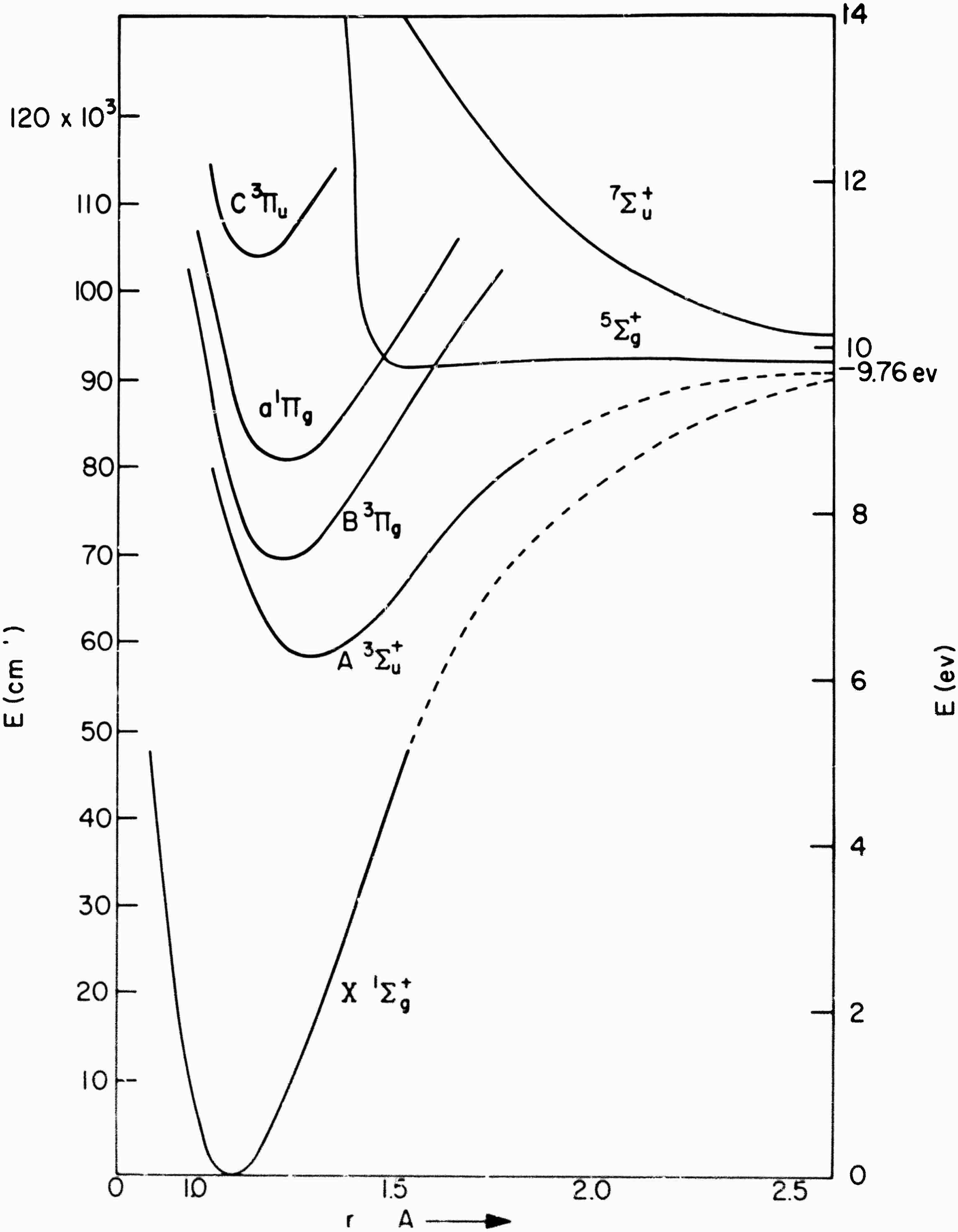


Fig. 1 POTENTIAL ENERGY DIAGRAM FOR N - N INTERACTIONS.
From: Vanderslice and others [J. Chem. Phys., 30, 129, (1959)]

The proposed reactions are:

$$N(^4S) + N(^4S) + M \rightarrow N_2\,(^5\Sigma_g^+) + M$$

$$N_2(^5\Sigma_g^+) \rightarrow N_2(a\ ^1\Pi_g) \rightarrow N_2(X\ ^1\Sigma_g^+) + h\nu$$

(Lyman-Birge-Hopfield bands)

$$N_2(^5\Sigma_g^+) \rightarrow N_2(B\ ^3\Pi_g) \rightarrow N_2(A\ ^3\Sigma_u^+) + h\nu \quad \text{(first positive bands)}$$

$$N(^4S) + N(^2D) \rightarrow N_2(C\ ^3\Pi_u) \qquad v = 4$$

$$N_2(C\ ^3\Pi_u) \rightarrow N_2(B\ ^3\Pi_g) + h\nu$$

At present the most plausible explanation for the active nitrogen afterglow appears to begin with the three-body collision reaction

$$N(^4S) + N(^4S) + M \rightarrow N_2(^5\Sigma_g^+) + M$$

involving the interaction between two ^4S nitrogen atoms. This process is known as the "preassociation theory" of active nitrogen and is seen to be the inverse of predissociation. The theory appears to be on a firm basis. Figure 1a is a diagram of potential curves of the N_2 molecule showing the $^5\Sigma_g^+$ state which crosses the B $^3\Pi_g$ state between the 12th and 13th vibrational levels.

1.6 DISSOCIATION ENERGY OF THE N_2 MOLECULE

Much of the early work on active nitrogen emphasized the existence of free nitrogen atoms. An examination of past work on the dissociation energy of molecular nitrogen reveals the existence of widely differing values of $D_o(N_2)$. The need to know the exact value for the heat of dissociation of molecular nitrogen in its ground state into two normal unexcited atoms in the $^4S_{3/2}$ state has prompted many recent investigations. Gaydon

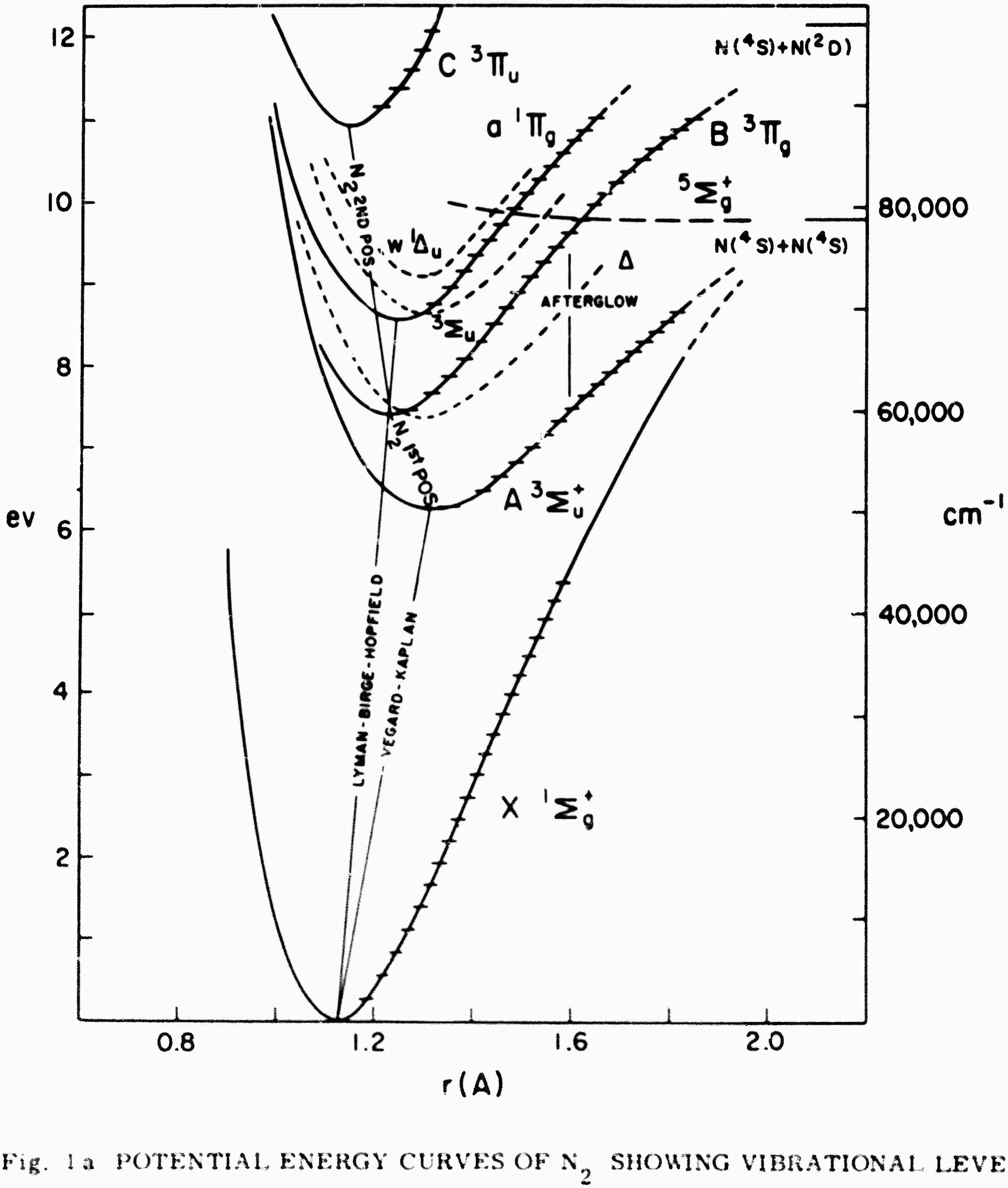


Fig. 1a POTENTIAL ENERGY CURVES OF N_2 SHOWING VIBRATIONAL LEVELS.
After: Kurweg and Broida [J. Molec. Spectros., 3, 388, (1959)]

("Dissociation Energies", London, Chapman and Hall, 1947) has summarized the three most likely values of 9.764, 8.573, and 7.383 ev for the dissociation energy of nitrogen and stated that the first appeared most likely.

The following experimental methods have been employed for the determination of $D_0(N_2)$: spectroscopic experiments, electron impact, shock wave and detonation studies, and thermal measurements. The data obtained from these various methods have indicated that the so-called high value of 9.764 ev for $D_0(N_2$, is probably correct. The acceptance of this value has aided greatly in the interpretation of the afterglow of active nitrogen, has provided an explanation of the newly discovered forbidden band systems in nitrogen, and has supplied a better understanding of the transitions occurring between the various excited electronic states of molecular nitrogen.

1.7 ABSORPTION OF ULTRAVIOLET RADIATION BY NITROGEN

The absorption spectrum of nitrogen in the vacuum ultraviolet is known to begin at 1450 A with the 0-0 band of the $^1\Pi_g$ - X $^1\Sigma_g^+$ system, the Lyman-Birge-Hopfield bands. Historically the discovery of the ultraviolet band system of nitrogen was made by Schumann (1903) who showed that nitrogen proved very transparent even beyond 1620 A. However it was found to absorb particular wavelengths very energetically. The emission bands of nitrogen consisted of a number of groups of bands of moderate photographic power diminishing toward the shorter wavelengths. Beyond 1850 A, Schumann was unable to detect any nitrogen bands. Twenty-one of the strongest emission band heads were in the interval $\lambda\lambda$ 1383-1871 A. These were first measured by Lyman (1911).

Worley and Jenkins (1938) have confirmed the existence of a molecular Rydberg series with a photoionization continuum starting at about 793 A corresponding to 1[illegible].503 ev and appearing at a path length of about 0.1 mm at N. T. P. Also in the shorter wavelength region good pictures of the Hopfield-Rydberg series converging at

TABLE 4. ABSORPTION SPECTRUM OF N_2

Region	Description
$\lambda\lambda$ 1450 - 1000 A	Series of narrow, discrete bands - Lyman-Birge-Hopfield bands. First identified by Lyman. Ref. Lyman (1911), Birge and Hopfield (1928), Watanabe (1958).
$\lambda\lambda$ 1000 - 800 A	Large number of strong, discrete bands forming numerous progressions, together with a molecular Rydberg series that converges to a limit at λ 796 A, corresponding to the 1st ionization potential of N_2. Ref. Worley and Jenkins (1938), Watanabe (1958).
$\lambda\lambda$ 800 - 650 A	Very strong band progressions and the Hopfield-Rydberg series converging to the second excited state $B\ {}^2\Sigma_u^+$ of N_2^+ at λ 661 A. Worley's Third Rydberg series of N_2 which converges to the $A\ {}^2\Pi_u$ state at 16.94 ev of N_2^+. Ref. Hopfield (1930) Phys. Rev., 35, 1133; Phys. Rev., 36, 789.
$\lambda\lambda$ 920 - 200 A	Blending of several continua, apparently continuous absorption. Ref. Ditchburn (1956), Astoin and Granier (1957).

ABSORPTION OF RADIATION BY N_2 (BRIEF SUMMARY)

Region	Description	Dissociation	Ionization
$\lambda\lambda$ 1450 - 1000 A	weak bands	none	none
$\lambda\lambda$ 1000 - 796 A	strong bands	none	$\lambda < 796$ A
$\lambda\lambda$ 800 - 661 A	Hopfield bands (strongest absorption)	none	$\lambda < 661$ A
	Worley's third Rydberg series	none	$\lambda < 732$ A
$\lambda\lambda$ 920 - 200 A	Blending of several continua of N_2	none	Ionization

661 A (18.67 ev) and appearing at equivalent lengths of 0.01 mm have been published by Takamine, Suga, and Tanaka (1938). All the data indicate that the bands are relatively sharp; no dissociation continua have been obtained. Table 4 summarizes some of the features of the absorption spectrum of nitrogen within various spectral regions.

Early contributions to our knowledge of the absorption of ultraviolet radiation by nitrogen were made by several other investigators. Their names are included in Figure 2, which shows the energy level diagram of the N_2 molecule and N_2^+. Later researches upon forbidden band systems in nitrogen, photoionization analysis of the N_2 molecule, absorption coefficients, and absorption cross sections have been made by Wilkinson and Mulliken (1959), Weissler and other (1959), Carleton and Lawrence (1958), Astoin and Granier (1957), Ditchburn (1956), Watanabe and Marmo (1956), Tanaka (1955), Wainfan and others (1955), Lee (1955), Ehler and Weissler (1955), Curtis (1954), and Clark (1952).

These investigations have provided potential information about fundamental processes and excitation reaction mechanisms for nitrogen in the upper atmosphere and ionospheric regions. Their measurements have assisted greatly in supplying data upon which to base a quantitative interpretation of the occurrence and vertical distribution of atomic nitrogen in the upper atmosphere and an explanation of the spectra of the night airglow and auroras. Table 5 shows the forbidden transitions in nitrogen from recently published data. Ogawa and Tanaka [J. Chem. Phys., 32, 754, (1960)] have observed new emission bands of forbidden systems in nitrogen in the vacuum ultraviolet which are in the same system of absorption bands studied by Wilkinson and Mulliken and shown in Table 5.

1.8 ABSORPTION COEFFICIENTS OF NITROGEN

Above 1200 A nitrogen is practically transparent. Experiments by Ditchburn (1956), Lee (1955), Watanabe and Marmo (1956), and Clark (1952) have been unable to establish the presence of a continuum

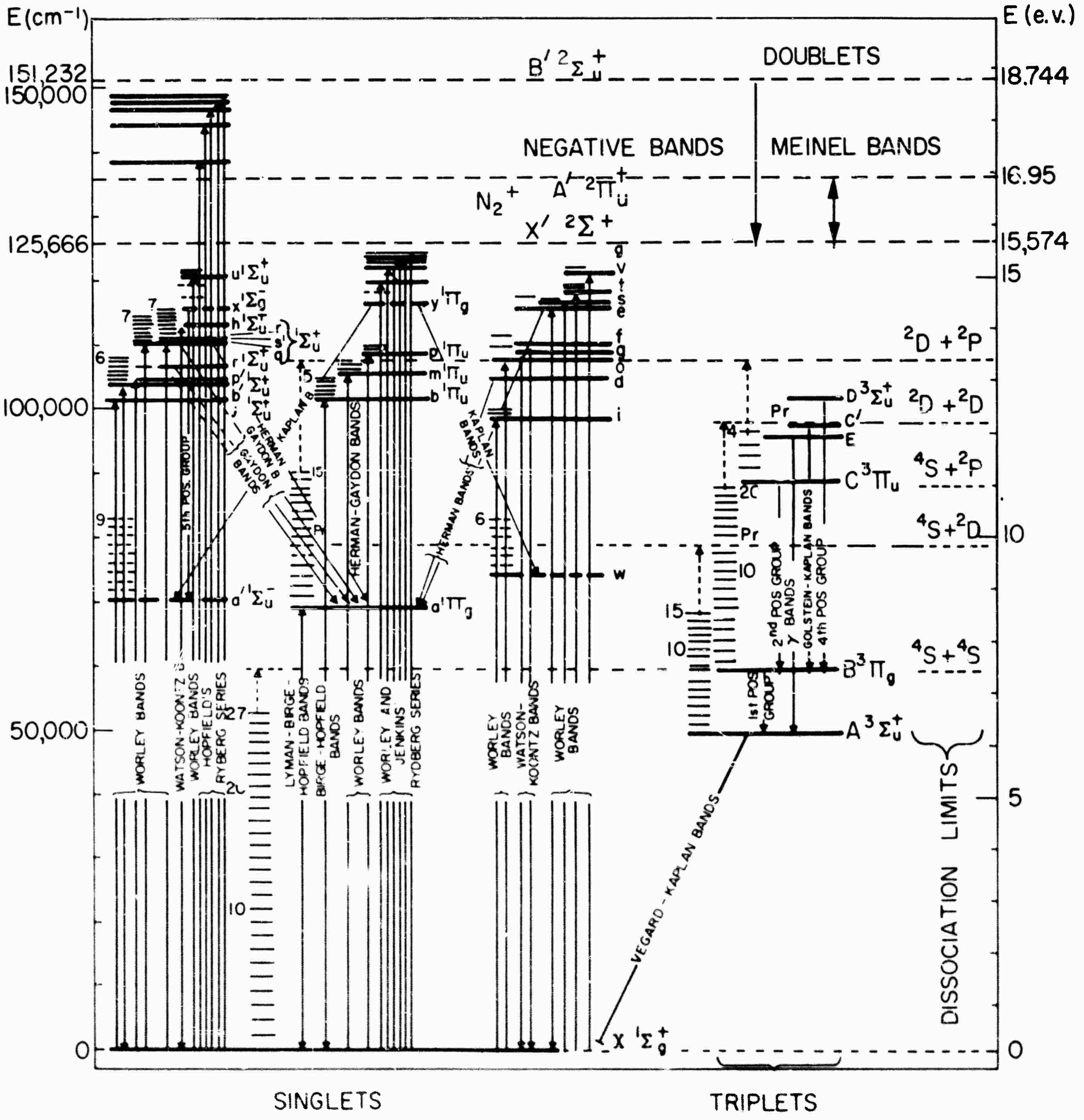


Fig. 2 ENERGY LEVEL DIAGRAM OF THE N_2 MOLECULE AND N_2^+ ION.

After: Herzberg, Spectra of Diatomic Molecules

TABLE 5. FORBIDDEN TRANSITIONS IN NITROGEN[a]

Transitions	Path Required (meter-atmos)	Relative Transition Probability	Mean Lifetime (sec)
$A\ {}^3\Sigma_u^+ - X\ {}^1\Sigma_g^+$	4	2.8×10^{-5}	2.6×10^{-2}
[Vegard-Kaplan Bands, J. Chem. Phys., 30, 773, (1959)]			
$a\ {}^1\Pi_g - X\ {}^1\Sigma_g^+$	0.2	3.1×10^{-4}	1.1×10^{-3}
[Lyman-Birge-Hopfield Bands, Astrophys. J., 126, 1, (1957)]			
$C\ {}^3\Pi_u - X\ {}^1\Sigma_g^+$	10^{-5}	3.6×10^{-4}	
[Tanaka System, J. Opt. Soc. Am., 45, 663, (1955)]			
$a'\ {}^1\Sigma_u^- - X\ {}^1\Sigma_g^+$	3.4	1.0×10^{-5}	4.0×10^{-2}
[Wilkinson-Mulliken System, J. Chem. Phys., 30, 773, (1959) ; ibid., 31, 674, (1959)]			
$Y\ {}^3\Sigma_u^- - X\ {}^1\Sigma_g^+$	3.4	1.5×10^{-5}	

(Wilkinson: Ogawa and Tanaka, A new system) (To be published)

(a) From Wilkinson and Mulliken [J. Chem. Phys., 31, 674, (1959)]

within the spectral region 850 to 1450 A. Ditchburn failed to detect any absorption with a path length of 150 centimeters of pure nitrogen at NTP. The cross-section is less than 10^{-22} cm^2. A number of "N_2-windows", that is regions of the spectrum a few angstroms wide, are known for which nitrogen the absorption is less than 1.6 cm^{-1}. The measurement of absorption coefficients and absorption cross-sections at the Lyman-β (1025.7 A) and Lyman-α (1215.66 A) wavelengths has a practical application since these radiations are strongly emitted by the sun and occur in the N_2-windows.

The intensity of absorption is expressed by the absorption coefficient, denoted by k (or the k value) in cm^{-1}. It is defined in accordance with Beer's Law from the relationship

$$I = I_o e^{-kx}$$

where I and I_o are the transmitted and incident light, respectively; x, expressed in centimeters, is the thickness of the absorbing gas-layer reduced to normal temperature and pressure. The cross-section σ is related to the absorption coefficient by the equation

$$\sigma = k/n_o$$

where n_o is the Loschmidt number, 2.69×10^{19} particles cm^{-3}.

Table 6 gives some recently determined values of absorption cross-sections σ for the Lyman-α and Lyman-β wavelengths. Recently Lee (1955) has shown that radiations having cross-sections of the order of 6×10^{-21} cm^2 in N_2 can penetrate through the upper atmosphere down to a level of about 120 km. This supports the view that nitrogen is comparatively transparent in the spectral region from 1000 to 1450 A. Ditchburn (1956) has estimated the penetration height at which radiation of a given photon energy would be attenuated by a fraction e of the original value to have a value of 125 to 150 km within the spectral range 920 to 200 A. This is the region where the following photoionization continua in nitrogen predominate:

$$N_2 + h\nu \xrightarrow{\lambda \leq 796 \text{ A}} N_2^+ + e^-$$

where the absorption cross-section σ, according to Curtis (1954), remains rather constant from about 1.0 to 1.3×10^{-17} cm^2 and

$$N_2 + h\nu \xrightarrow{\lambda \leq 738 \text{ A}} N_2^+ \text{ (excited)} + e^-$$

$$N_2 + h\nu \xrightarrow{\lambda \leq 661 \text{ A}} N_2^+ \text{ (excited)} + e^-$$

where the absorption cross section σ has been calculated by Bates and Seaton (1947) to be about 9.3×10^{-18} cm^2.

Figure 3 shows absorption coefficients obtained by a number of investigators for wavelengths below λ 1000 A. The absorption in this region is regarded as somewhat uncertain. The values should be considered as semi-quantitative rather than absolute. The Lyman-Birge-Hopfield absorption bands of N_2 may be observed in Figure 4.

TABLE 6. UPPER LIMIT ABSORPTION CROSS SECTIONS OF N_2

Wavelength	Cross-sections σ cm^2	Reference
λ 1215.66 A	6×10^{-23} cm^2	Ditchburn and others (1954)
Lyman-α	2.2×10^{-19} cm^2	Weissler and others (1952)
λ 1025.6 A	3×10^{-19} cm^2	Clark (1952)
Lyman-β	1.1×10^{-20} cm^2	Lee (1955)
λ 972.6 A	3.7×10^{-21} cm^2	Watanabe and Marmo (1956)
Lyman-y	1.45×10^{-16} cm^2	Clark (1952)
λ 584.3 A	1.8×10^{-17} cm^2	Clark (1952)
He I Resonance Line	1.3×10^{-17} cm^2	Curtis (1954)
	1.9×10^{-17} cm^2	Watanabe (1959)
λ 303 A Helium I I Resonance Line	4.6×10^{-18} cm^2	Curtis (1954)
λ 150 A	3×10^{-18} cm^2	Curtis (1954)

1.9 EXPERIMENTAL EVIDENCE FOR THE PRESENCES OF ATOMIC NITROGEN IN THE UPPER ATMOSPHERE

During the period of the 1940's and early 1950's the presence of

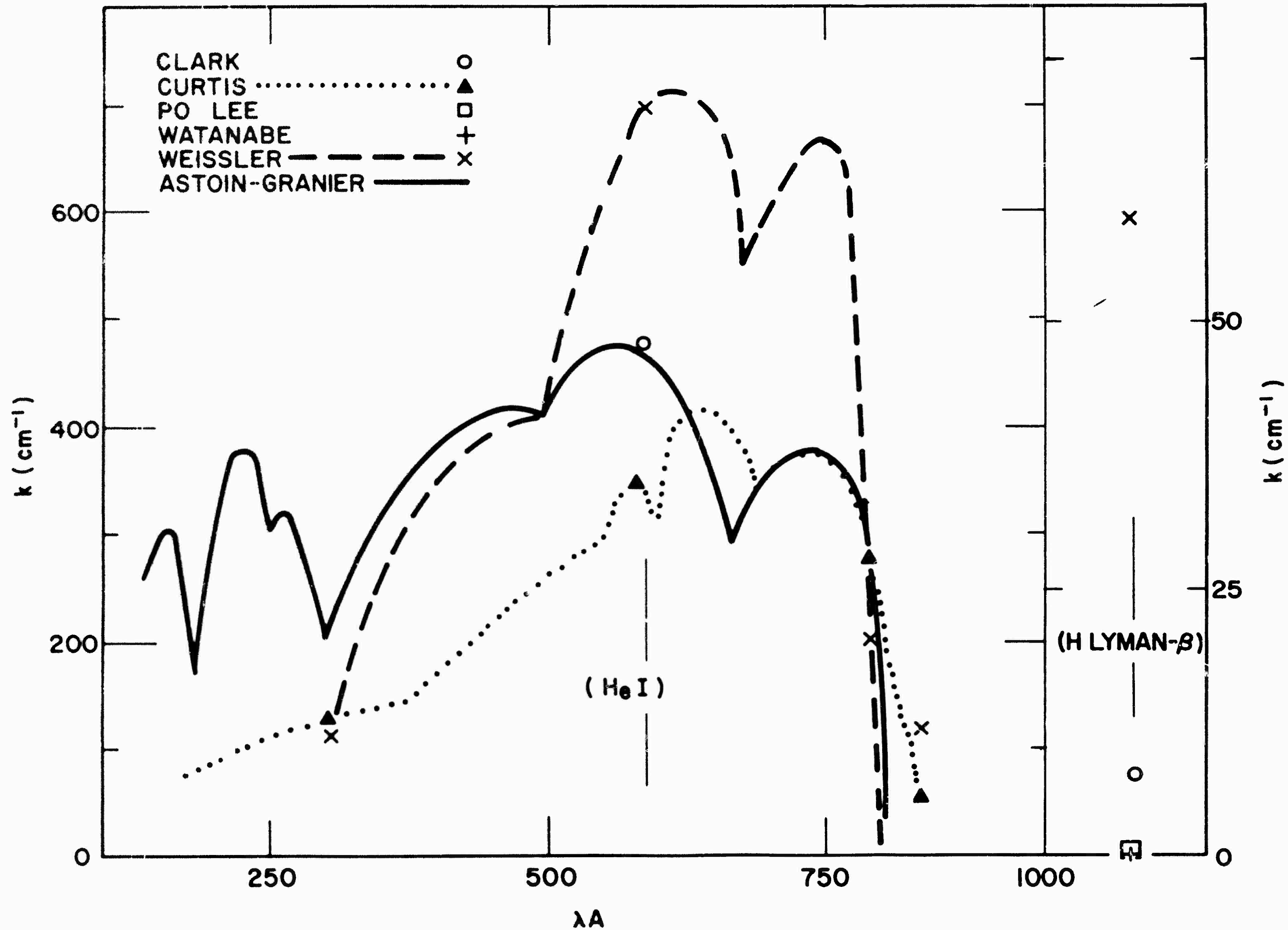
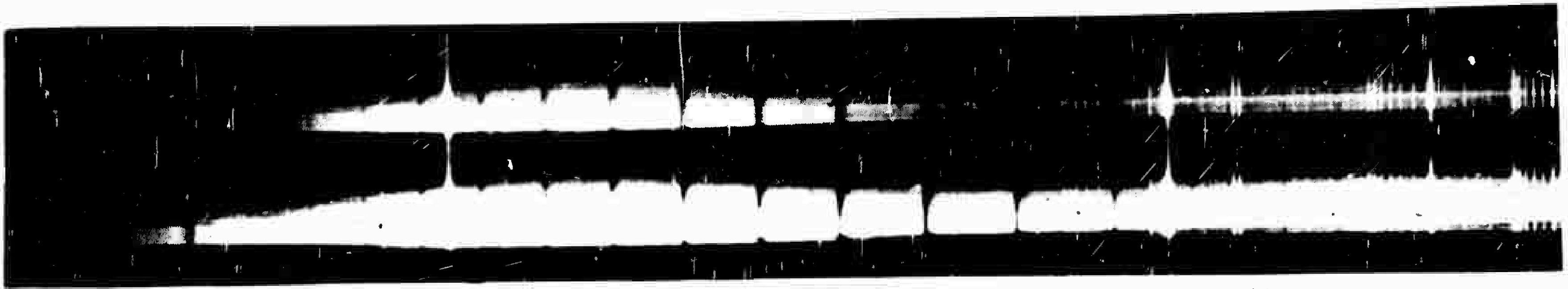


Fig. 3 ABSCRPTION COEFFICIENTS FOR N_2 IN THE EXTREME ULTRAVIOLET.

After: Astoin-Granier, [Compt. rend., 244, 1350, (1957)]



$$a^1\Pi_g \leftarrow X^1\Sigma_g^+$$

Fig. 4 LYMAN-BIRGE-HOPFIELD ABSORPTION BANDS OF N_2
Courtesy of Dr. Yoshio Tanaka

atomic nitrogen in the upper atmospheric regions was a controversial subject. The following objections have been raised that made it difficult to believe that atomic nitrogen could be a constituent of the upper atmosphere at normal times. (a) Nitrogen was regarded as chemically inert. (b) There was no simple photodissociation process for molecular nitrogen analogous to that of molecular oxygen. (c) Molecular nitrogen bands are present in the spectrum at high altitudes in sunlit auroras. (d) The dissociation efficiency is very low outside of the auroral region. (e) Molecular nitrogen does not have an observable continuum in the spectral region where the solar flux is sufficiently intense to produce much dissociation, as in the case of molecular oxygen. It is generally agreed that the observance of the presence of atomic nitrogen in the twilight and night sky, in the absence of auroral and magnetic disturbances, is necessary to establish it as a regular component in the upper atmosphere.

1.9.1 EXPERIMENTAL EVIDENCE FOR THE PRESENCE OF N I IN AURORAS

The presence of N I in the upper atmosphere was first announced by Slipher and Sommer at the 42nd meeting of the American Astronomical Society held in Ottawa, Canada, 26-29 August 1929. They reported their observations on the spectrum of the auroral display of 7 July 1928 observed at the Lowell Observatory. The line which appeared near λ 5206 A in the spectrum of this unusual aurora was interpreted on the basis of the quantum theory as belonging to the spectrum of the neutral nitrogen atom. Later Slipher obtained the forbidden λ 5206 A line $^4S-^2D$ of N I on a spectrogram of an aurora on 29 May 1932.

In 1938 Bernard observed the lines at λ 3466.5 A in the spectra of diffuse auroras which led him to accept the presence of ^2P metastable nitrogen atoms in the upper atmosphere. During the year 1941 Dufay,

Tcheng Mao-Lin, and Gauzit published several papers on auroras observed at the Observatory of Haute-Provence. The radiation of the observed wavelength λ 5199 A was interpreted as establishing definite evidence of the forbidden doublet N I λλ 5197.8 – 5200.1 A ($^4S-^2D$) in the auroral spectrum. In Table 7 the observations of the occurrence of nitrogen atoms in the auroral region are tabulated.

1.9.2 EXPERIMENTAL EVIDENCE FOR THE PRESENCE OF N I IN THE TWILIGHT AND NIGHT SKY

Observation of the forbidden radiations of atomic nitrogen at wavelengths λλ 5199, 3466, and 10410 A is now considered a regular feature in the spectra of auroras. Figure 5 supplied by the Yerkes Observatory shows the strong forbidden line of N I at 5200 A taken during an auroral display. Figure 6 shows the presence of the forbidden N I ($^4S-^2D$) in the spectrum of an aurora at the Geophysical Institute, College, Alaska.

Experimental evidence for the occurrence of atomic nitrogen in the night sky in the absence of magnetic and auroral disturbances at first seemed less convincing than for its presence in auroral spectra. The light of an aurora is generally regarded to be produced differently from that of the airglow. An aurora is assumed to be caused by charged solar particles entering the earth's atmosphere from outer space. The auroral light is then emitted mainly by the bombarded atmospheric gases and sometimes by protons which have captured electrons in the incident stream.

The generally accepted theory is that the airglow results from photochemical reactions occurring in the upper atmosphere, caused by absorption of solar energy during the day and slowly emitted during the night. The airglow is enhanced at twilight. There are diurnal and

TABLE 7. THE DISCOVERY AND IDENTIFICATION OF ATOMIC NITROGEN IN THE AURORAL REGION

Observer	Date	Place	Discovery	Reference	Remarks
Slipher and Sommer	1929	Lowell Observatory	λ 5206 A in auroral region	Naturwiss., 17, 802, (1929); Publ. Am. Astron. Soc., 6, 280, (1931); Mon. Not. Roy. Astron. Soc., (London), 93, 664, (1933)	Interpreted as belonging to the spectrum of the neutral nitrogen atom
Bernard	1938	Tromso	λ 3466.5 A line observed	J. Phys. Radium, 9, 157S, (1938); Nature, 141, 1140, (1938), Phys. Rev., 55, 551, (1939); Ann. Astrophys., 4, 13, (1941); Ann. geophys., 3, 53, (1947)	Presence of ^2P metastable nitrogen atoms in the spectra of auroras
Vegard, Vegard and Tonsberg, Vegard and Kvifte	1938	Tromso	Obtained the line λ 3464.4 A	Nature 142, 670, (1938); Geopys. Publ. Oslo, 13, No. 5, (1941); ibid., 16, No. 7 (1945); Physica, 12, 606, (1946)	Previously regarded as the head of the 2nd pos. group

TABLE 7. THE DISCOVERY AND IDENTIFICATION OF ATOMIC NITROGEN IN THE AURORAL REGION

(Continued)

Observer	Date	Place	Discovery	Reference	Remarks
Dufay and Mao-Lin	1941	Observatory of Haute-Provence	Observed the radiation λ 5199.4 A	Compt. rend, 213, 692, (1941); Cahiers Phys., 8, 51, (1942); Ann. astrophys., 6, 81, (1943)	Interpreted as the forbidden doublet of N I $\lambda\lambda$ 5197.8-5200.1 A $^4S-^2D$
Gotz	1941	Observatory Arosa	Found the lines λ 5199 A and λ 3467 A	Naturwiss., 29, 690 (1941); ibid., 30, 752, (1942); Experimenta, 3, 185, (1947)	Confirms presence of N I in auroras
Barbier and Williams	1950	Geophysical Observatory Univ. Alaska	The line λ 3466 A in spectrum of aurora	J. Geophys. Res., 55, 401, (1950)	Confirm the presence of N I line 3467 A
Gartlein	1950	Cornell Univ.	The sharp forbidden N I lines at λ 5199 A observed	Trans. Ann. Geophys. Union, 31, 18, (1950)	Brief description of features of auroral spectra
Petrie	1950	Univ. Saskatchewan	Infrared lines of N I observed	J. Geophys. Res., 55, 143, (1950); Phys. Rev. 77, 720, (1950)	Considerable amount of N_2 dissociated at 60 miles

TABLE 7. THE DISCOVERY AND IDENTIFICATION OF ATOMIC NITROGEN IN THE AURORAL REGION (Continued)

Observer	Date	Place	Discovery	Reference	Remarks
Meinel	1948	Lick Observatory	Infrared spectra of N I observed	Publ. Astron. Soc. Pacific, 60, 373, (1948); Astrophys. J., 113, 585, (1951)	$\lambda\lambda$ 8684 and 8714 A observed
Robley, Bricard, and Kasler	1948-1949	Observatory d Abisko	Radiation at λ 5205 A was strong	Ann. geophys., 6, 66, (1950)	Confirmed results of Slipher, Gotz, and Dufay
Vegard, Vegard and Kvifte	1950	Oslo, Norway	N I doublet $\lambda\lambda$ 5197.7–5200.8 A very distinct	Compt. rend., 230, 1884, (1950); Ann. geophys. 6, 157 (1950); Geofys. Publ. Oslo, 18, No. 3, (1951); also, No. 8, (1952)	The presence of N I and N II lines definitely established
Petrie and Small	1952	Univ. Saskatchewan	$\lambda\lambda$ 5198–5201 A appear only in high altitude auroras	Astrophys. J., 116, 443, Phys. Rev. 87, 1002, (1952); Can. J. Phys., 31, 911, (1953)	Wavelengths and Identifications obtained
Dufay, M.	1957	Observatory of Haute-Provence	Doublet $^4S-^2D$ of N I present in spectrum of low latitude aurora	Compt. rend., 245, 1648, (1957)	Appeared with exceptional intensity
Barbier	1958	Observatory of Haute-Provence	Forbidden N I line at 5200 A frequently observed	Ann. geophys. 14, 334, (1958)	Many photometric measurements made

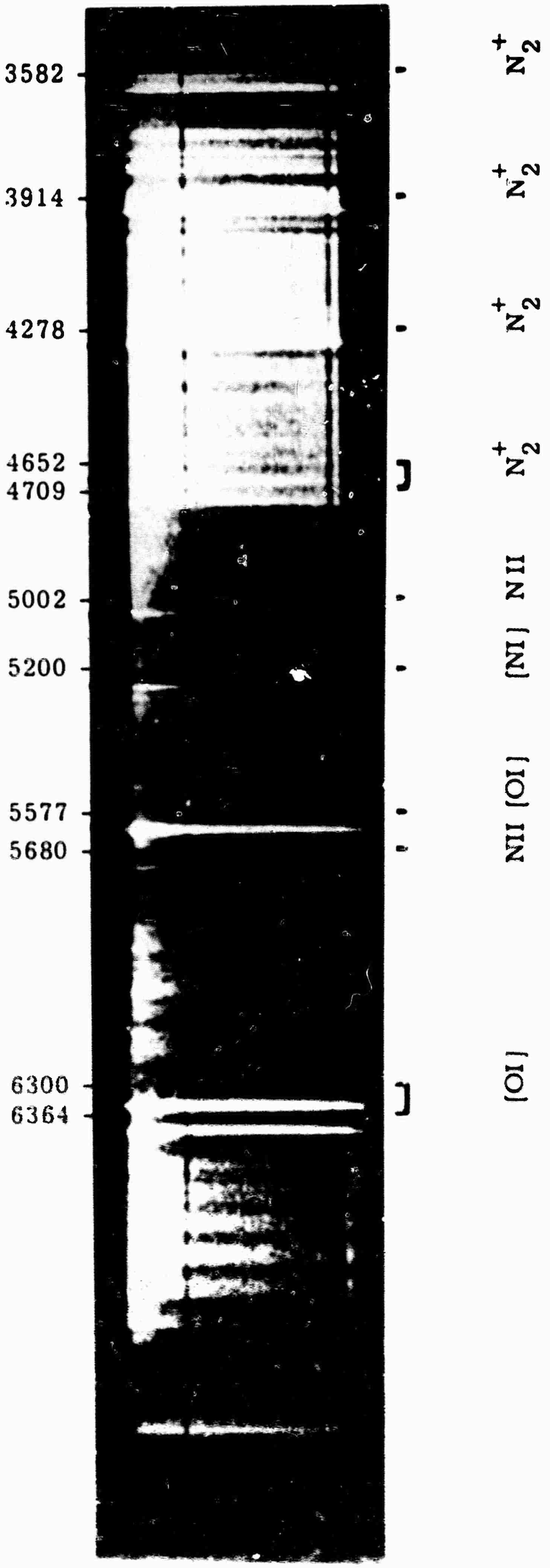
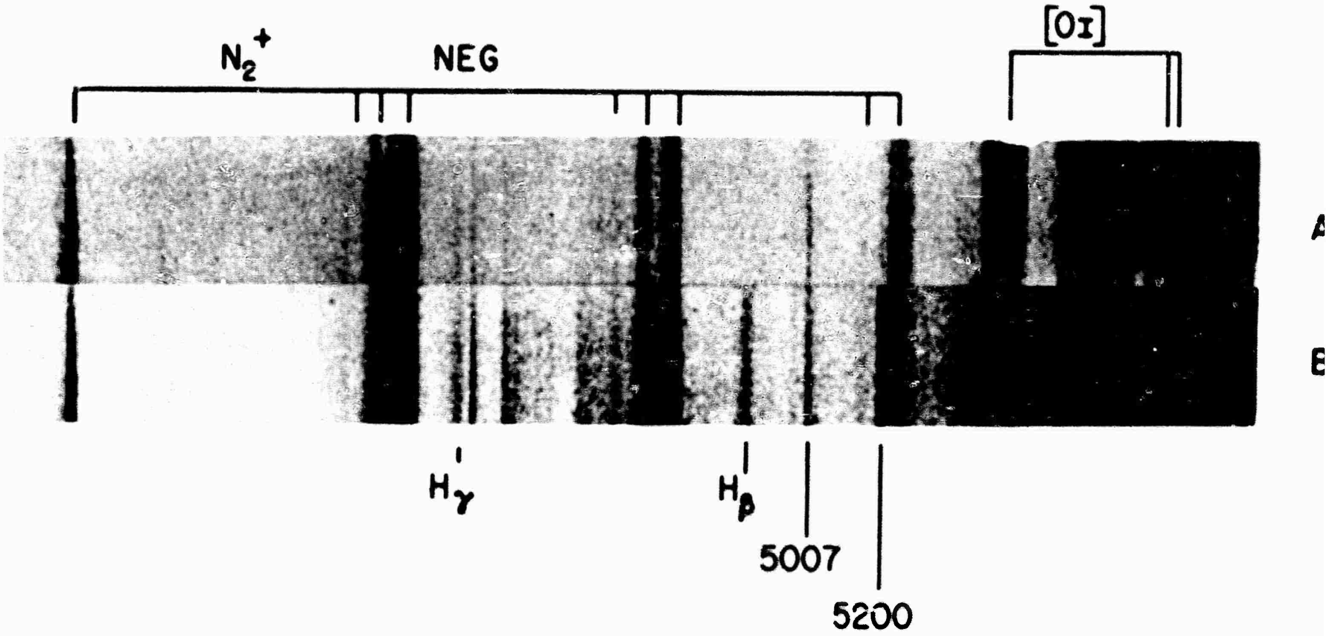


Fig. 5 FORBIDDEN LINE OF N I AT 5200 A. TAKEN DURING AN AURORAL DISPLAY AT YERKES OBSERVATORY. Courtesy, Dr. J. W. Chamberlain



SPECTRA OF: A, BRIGHT AURORAL RAY
B, UPPER PART OF RAY

Fig. 6 AURORAL SPECTRUM OF AN AURORA AT COLLEGE, ALASKA.
Courtesy of D. C. T. Elvey

seasonal intensity variations; there are also irregular variations or "patchiness" during the night sky.

The photography of the spectrum of the night sky radiations is difficult because of the low surface brightness of the sky. The light is so weak th' 'long exposures and low dispersions are necessary. Exposures of fr m eight to thirty hours are required. A list of some of the observations of atomic nitrogen in the twilight and night sky is given in Table 8.

In 1945 Stebbins, Whitford, and Swings reported the identification of the forbidden $^2D-^2P$ multiplet of N I in the infrared radiation which they detected in the night sky. Herman, Herman, and Gauzit also were able to photograph the forbidden $^2D-^2P$ radiation of atomic nitrogen in the spectrum of the night sky in the near infrared. This confirmed a prediction made by Gauzit in 1941 that nitrogen should be found in the atomic state in the upper atmosphere.

Courtes (1950) announced that he had observed the forbidden transition $^2D-^4S$ of N I in the spectrum of the twilight sky which hitherto had only been observed in the auroral spectrum. In a paper published in 1951 M. Dufay reported the results of his observations of the night sky and twilight. The forbidden line $^2D-^4S$ of N I appeared on 25 of the spectrograms. The line had a greater intensity during summer months in the sky at twilight than after twilight. This phenomenon was not observed during winter months. The wavelength was determined to be 5199.1 A from an average of 18 measurements. The line appeared consistently in the photographs during twilight. The emission is not correlated with geomagnetic disturbances. Later in 1959 Dufay reported that the $^4S-^2D$ (5199 A) line of the neutral nitrogen atom was observed regularly in the night sky spectra during 1958-1959. The appearance of

TABLE 8. EXPERIMENTAL EVIDENCE FOR THE PRESENCE OF N I IN THE TWILIGHT AND NIGHT SKY

Observer	Date	Place	Discovery	Reference	Remarks
Herman, Herman, and Gauzit	1942	Observatory of Lyon	The forbidden doublet $^2P-^2D$ of the N I atom (λ 10410-10401 A) observed	Cahiers phys. 2, No. 12, 46, (1942); J. Phys. radium, 6, 182, (1945); Nature, 156, 114, (1945)	The presence of N I in the upper atmosphere indicated. Predicted that the $^2P-^4S$ line at 3466 A should be observed
Stebbins, Whitford, and Swings	1945	Mt. Wilson Observatory	New infrared radiation near λ 10440 $\pm$ 25 A observed	Astrophys. J., 101, 39, (1945)	The possible presence of N I near λ 10440 A considered
Meinel	1948	Lick Observatory	$\lambda\lambda$ 8684-8714 A	Publ. Astron. Soc. Pacific, 60, 373, (1948)	N I lines present in spectrum
Rodionov and Pavlova	1949	A. A. Zhdanov State Univ. Leningrad	The band 10400 A most intense in the interval $\lambda\lambda$ 11000-8000 A	Doklady Akad. Nauk, S. S. S. R., 65, 831, (1949)	The band attributed to recombination of N I atoms
Courtes	1950	Observatory of Haute-Provence	The ray $^4S-^2D$ of atomic nitrogen observed at twilight	Compt. rend., 231, 62, (1950)	Hitherto had only been in auroral light

TABLE 8. EXPERIMENTAL EVIDENCE FOR THE PRESENCE OF N I IN THE TWILIGHT AND NIGHT SKY

(Continued)

Observer	Date	Place	Discovery	Reference	Remarks
Dufay, M.	1951	Haute-Provence Observatory	Forbidden $^4S-^2D$ line of N I observed in night sky and at twilight	Compt. rend., 233, 419, (1951); Mem. Soc. Roy. Sci., Leige, 12, 141, (1952); Ann. Phys., 8, 813, (1953); Compt. rend., 236, 2160, (1953) ibid, 248, 2505, (1959)	The line 5199 A attributed to atomic nitrogen
Laukasheny and Krasovskii	1951	Astrophys. Observatory, Crimea	The doublet $^2P-^2D$ identified in night sky spectra	Doklady Akad. Nauk, S.S.S.R., 79, 241, (1951)	Attributed to atomic nitrogen
Krasovskii and others	1958	Zvenigarod	The N I line at λ 5200 A photographed	Ann. geophys., 14, 356, (1958)	No aurora or magnetic disturbances at the time
Zeiikoff and others	1958	White Sands, N. Mexico	Release of ethylene from rocket at 105 km produced luminescent CN bands	J. Geophys. Res., 63, 31, (1958)	Reaction attributed to presence of atomic nitrogen at 105 km
Kvifte	1959	Ås Norway	5200 A appeared on spectra of the night glow	Geofys. Publikajoner Norvegica, XX, No. 12, (1959)	No auroral activity visible on nights when night glow spectra were taken

TABLE 3. EXPERIMENTAL EVIDENCE FOR THE PRESENCE OF N I IN THE TWILIGHT AND NIGHT SKY
(continued)

Observer	Date	Place	Discovery	Reference	Remarks
Blackwell, Ingham, and Rundle	1960	Chalcaltaya (latitude -60°)	Existence of 5200 A on spectra	Astrophys. J., 131, 15, (1960)	Demonstrated the existence of N I in night sky without any doubt

this forbidden radiation in the light of the night sky may be discerned in Figure 7 which is a photograph taken by Dufay.

According to Garstang (1952) the upper term for the N I doublet ($\lambda\lambda$5200.7-5198.5 A) has a lifetime of about 26 hours. It would seem reasonable to suppose that the daytime resonance excitation should persist during the night. The forbidden transitions for the nitrogen atom are shown in Figure 8.

1.9.3 DIRECT EVIDENCE FROM ROCKET FLIGHT

Additional data for the occurrence of atomic nitrogen in the upper atmosphere which might be considered as direct confirmatory evidence have been obtained from rocket flights. During February 1957 Zelikoff and his co-workers of the Geophysics Research Directorate of the Air Force Cambridge Research Center, Air Research and Development Command, released ethylene gas at night at altitudes of 105 and 143 kilometers in a rocket flight at White Sands, New Mexico.

The chemiluminescent bands of CN observed at 105 km were interpreted to establish the presence of atomic nitrogen at altitudes of slightly over 100 kilometers. This result was unusual since theoretical calculations have lead upper atmospheric scientists to believe that appreciable amounts of atomic nitrogen would only be found above 150 kilometers. In a communication presented before the assembly of the International Union of Geodesy and Geophysics held at Toronto, Canada, September 1957, Krasovskii and his associates reported that they had photographed several night sky spectra at Zvenigarod in which the N I line at 5200 A is shown although there was no aurora or magnetic disturbance at the time.

1.10 THEORETICAL MECHANISMS TO ACCOUNT FOR THE OCCURRENCE OF ATOMIC NITROGEN IN THE UPPER ATMOSPHERE

Enough experimental evidence has been obtained in recent years

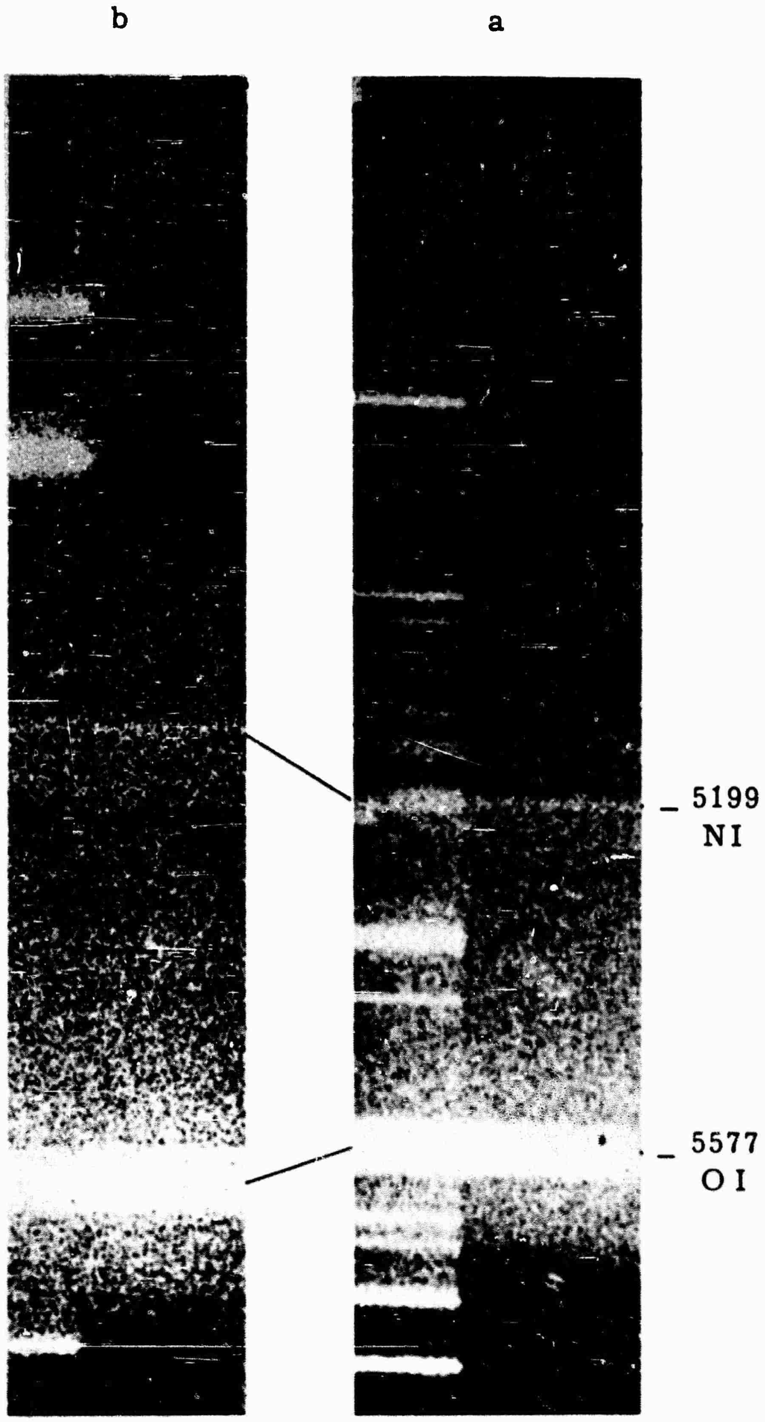


Fig. 7 5199 A LINE OF N I OBSERVED IN THE NIGHT SKY.

Courtesy of Dr. Maurice Dufay, University of Paris

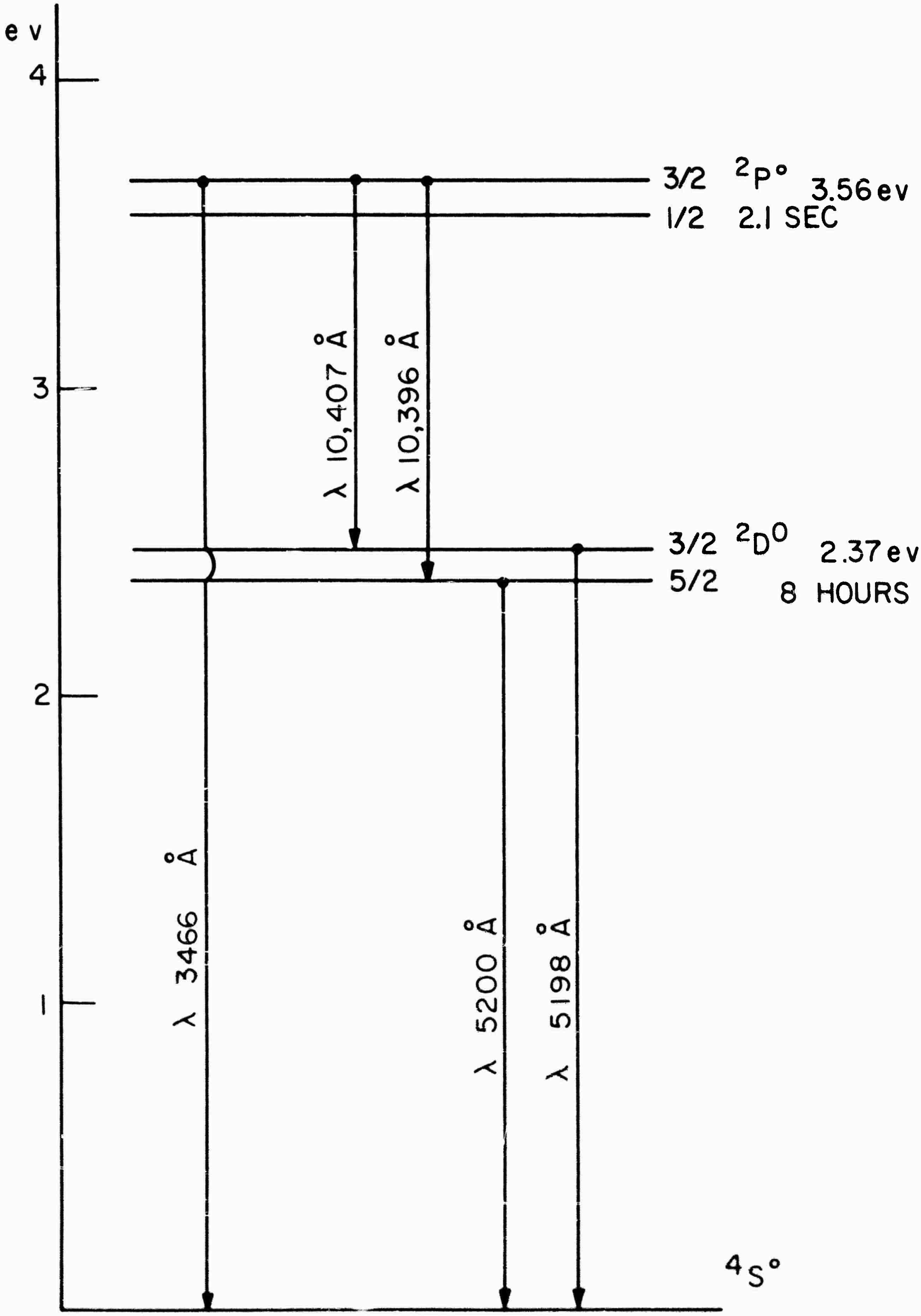


Fig. 8 FORBIDDEN TRANSITIONS FOR THE NITROGEN ATOM.

to establish that atomic nitrogen is present in the upper atmosphere and that molecular nitrogen is at least partially dissociated, although not by a primary direct process as in the case of molecular oxygen. Three processes have been proposed to account for the production of nitrogen atoms in the upper regions of the atmosphere. These mechanisms are: (a) the predissociation theory; (b) the ionization recombination mechanism; and (c) the ion charge exchange process. The possibility of the ionization of molecular nitrogen as a process in the ionosphere, and the subsequent formation of nitrogen atoms, has largely removed many of the early objections raised against the presence of atomic nitrogen as an atmospheric constituent.

1.10.1 THE PREDISSOCIATION THEORY

Herman (1943 and 1945) found that under certain conditions of discharge there was a breaking off above the level $v' = 6$ in the Lyman-Birge-Hopfield (a – X) bands of nitrogen. Herzberg and Herzberg were able to confirm this observation in nitrogen excited at low pressures in a high-frequency electrodeless discharge. They pointed out that predissociation occurs and that the predissociation limit is between the levels $v' = 6$ and 7 of the $a\text{-}\Pi_g$ state. The production of nitrogen atoms by predissociation in the (a – X) bands is independent of the correctness of the value of $D_o(N_2)$. However if the high value of 9.764 ev is accepted, the predissociation would lead to formation of the two normal ^4S atoms of nitrogen.

The process is represented as follows:

$$N_2(X\ ^1\Sigma_g^+) + h\nu \xrightarrow{\lambda\lambda 1150-1250\ \text{A}} N_2(a\ ^1\Pi_g)$$

$$N_2(a\ ^1\Pi_g) \longrightarrow N(^4S) + N(^4S)$$

The formation of nitrogen atoms according to the predissociation mechanism is considered to occur over a considerable altitude range since absorption of oxygen molecules is comparatively weak in the spectral range λλ 1150-1250 A. Qualitatively this process is believed to be effective at low altitudes, below about 140 km. Figure 9 is a summarizing diagram which shows the metastable states of the N_2 molecule and the excited states of the nitrogen molecule ion N_2+.

1.10.2 THE IONIZATION-DISSOCIATIVE RECOMBINATION MECHANISM

Production of atomic nitrogen in the high atmosphere by a dissociative recombination process was suggested independently and simultaneously by S. K. Mitra (1951) and Bates (1952). In this process the primary reaction is the production of nitrogen molecule ions, N_2^+, by absorption of ultraviolet radiation in the spectral range $\lambda \leq 795$ A. The molecular ions thus formed may undergo dissociative recombination with electrons to yield nitrogen atoms in the F-region of the ionosphere.

$$N_2 + h\nu \xrightarrow{\lambda \leq 795 \text{ A and } \lambda < 661 \text{ A}} N_2^+ (X^1) + e^-$$

$$N_2^+(X') + e^- \longrightarrow N(^2P) + N(^2D)$$

This process is considered to be operative at high altitudes, above about 140-150 km.

The dissociative recombination coefficient has been measured in the laboratory by A. C. Faire and K. S. W. Champion [Phys. Rev., 113, 1, (1959)] who obtained a value of 4×10^{-7} cm^3 sec^{-1}.

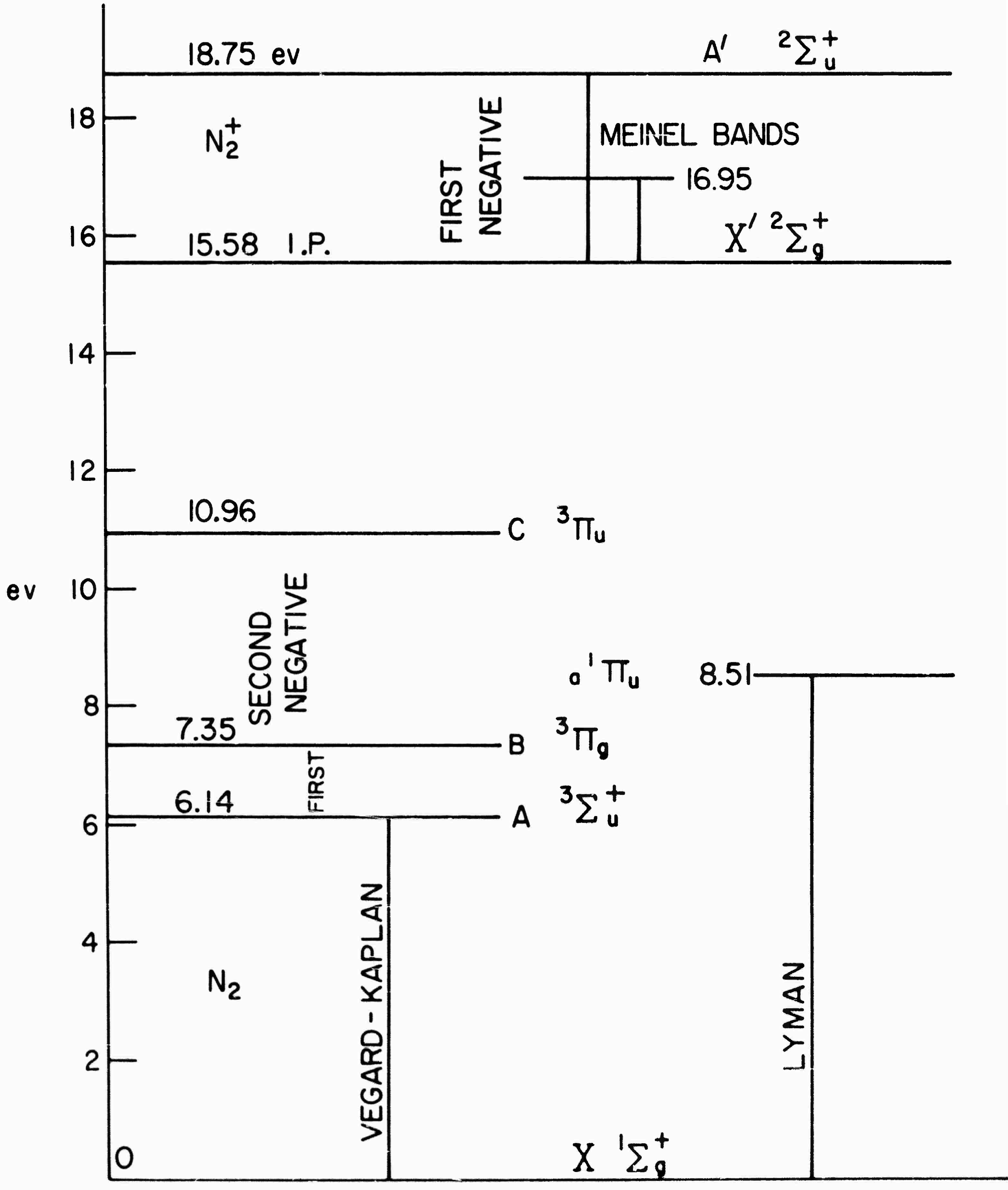


Fig. 9 ENERGY LEVEL DIAGRAM OF METASTABLE STATES OF THE N_2 MOLECULE

1.10.3 ION-ATOM INTERCHANGE COLLISION PROCESS

Atomic nitrogen may also be formed in upper ionospheric regions by the ion-atom interchange collision process.

$$0^+ + N_2 \rightarrow NO^+ + N$$

$$N_2^+ + 0 \rightarrow NO^+ + N$$

These processes outlined above have been studied theoretically by Bates (1952) and by Nicolet (1954, 1959) who have found the mechanisms satisfactory by considering the rate coefficients for the various reaction mechanisms, absorption coefficients, the photons available at the top of the earth's atmosphere (2×10^9 photons cm^{-2} sec^{-1}), the ionization rate coefficient at zero optical depth (4.4×10^{-8} sec^{-1}), the life-time of a nitrogen atom at various altitudes, and other factors. Lyman-alpha through predissociation is considered to be able to dissociate nitrogen by the Herzberg-Herzberg process. This radiation has been observed to penetrate to a depth of about 75 km in the earth's atmosphere.

Nitrogen atoms once formed in the upper atmosphere may disappear through a number of reactions

$$N + N \xrightarrow{k_1} N_2 + h\nu$$

$$N + O + M \xrightarrow{k_2} NO + M$$

$$N + N + M \xrightarrow{k_3} N_2 + M$$

$$N + NO \xrightarrow{k_4} N_2 + O$$

At λ 852 A atomic nitrogen has its first ionization potential (14.52 ev). The theoretical absorption coefficient is about 9×10^{-18} cm^2 for this wavelength. In addition to the preceding reactions atomic nitrogen immediately above the transition region for the dissociation of molecular oxygen (100-110 km) may react ultimately with molecular oxygen according to the process

$$N + O_2 \longrightarrow NO + O$$

and may disappear by the reaction

$$NO + N \longrightarrow N_2 + O$$

Through the latter reactions it may be seen that there is a definite inter-relationship between atomic nitrogen and nitric oxide. There are complexities involved in the photochemical and dynamical mechanisms for the degree of dissociation of molecular nitrogen and the various subsequent reactions of nitrogen atoms with other atmospheric species. At present it is difficult to formulate exact and preferential reaction processes to the exclusion of others. It is rather certain that atomic nitrogen moves downward, in accordance with Dalton's law of diffusion, from the region of formation before processes leading to the ultimate reconversion to molecular nitrogen occur.

1.11 THE VERTICAL DISTRIBUTION OF ATOMIC NITROGEN

Only a few direct observations have been made of the altitude and distribution of atomic nitrogen in the upper atmosphere. According to M. Dufay [Ann. phys., 8, 813, (1953)] the apparent emission height of λ 5199 A of N I in the night sky is between 90 and 125 km. Zelikoff and his co-workers (1958) concluded from a rocket experiment in which

ethylene gas was released that the altitude of the red color of the cloud, caused by $N-C_2H_4$ and attributed to the presence of atomic nitrogen, was 105 km.

Table 9 gives some statements contained in the literature concerning the vertical distribution of atmospheric atomic nitrogen. There are wide differences of opinions both as to the altitude and concentration at various altitudes. The early estimates were probably arrived at by intuitive reasoning by comparison with that of the vertical distribution of atomic oxygen. There had been many calculations made of the altitude of emission of the forbidden green line $\lambda 5577$ A of O I.

The later deductions of Nicolet, Bates, and Seaton have been more conservative in regard to the amount of nitrogen atoms in the vertical distribution. The trend of these later theoretical analyses appears to regard atomic nitrogen as only a minor atmospheric constituent in the thermosphere and probably also at higher altitudes.

1.12 MODEL ATMOSPHERES

Many model atmospheres have been proposed for the vertical distribution of the atmospheric components in order to deduce a temperature and density profile with altitude. The vertical distribution of atomic nitrogen has often been included in these profiles.

Deb (1952) calculated a vertical distribution profile for the probable distribution of atomic nitrogen in the upper atmosphere. Two mechanisms for production of atomic nitrogen were considered: (a) the predissociation theory of Herzberg and Herzberg; and (b) the dissociative recombination mechanism of Mitra and of Bates. The method of calculation was the one adopted by Penndorf [J. Geophys. Research, 54, 7, (1949)] and based upon photochemical equilibrium. Both Spitzer (1949) and Nicolet (1954) have shown that atomic nitrogen must be distributed by diffusive equilibrium to give acceptable results.

Havens, Friedman, and Hulburt [Phys. Soc., (London), The Physics of the Ionosphere, Report of the 1954 Cambridge Conference, pp. 237-244] have deduced an upper atmospheric model for which the percentages of O_2 and O were based on measurements made from about 100 to 130 km on the Aerobee 16 rocket flight [Phys. Rev., 98, 1594, (1955)]. The percentages of N_2 and N were estimated values.

In order to supply the molecular weights of air at high altitudes for the extension of the U. S. Standard Atmosphere, Miller [J. Geophys. Research, 62, 351, (1957)], deduced an atomic nitrogen distribution by assuming diffusive equilibrium above 180 km, using the distribution of O_2 and O obtained by Byram, Chubb, and Friedman (1955) and the scale height and density profiles adopted by the Working Committee for the extension of the U. S. Standard Atmosphere. Kallman, White, and Newell [J. Geophys. Research, 61, 513, (1956)] have published a model atmosphere which Kallmann and White also presented before the Working Committee for the extension of the U. S. Standard Atmosphere. It was assumed that N_2 begins to dissociate appreciably only above 220 km since at that time no atomic ions of nitrogen had been observed below 219 km. Nitrogen was considered to be approximately 75 percent dissociated at the critical level.

A. P. Mitra (1953, 1954) has considered atomic nitrogen as a constituent of the F_1 region. Three models were derived. The first was an idealistic case of photochemical equilibrium for which the distribution of atomic nitrogen was given by

$$n(N) = \left[\frac{J \quad n(N_2)}{K} \right]$$

TABLE 9. STATEMENTS IN THE LITERATURE ABOUT THE VERTICAL DISTRIBUTION OF ATOMIC NITROGEN

Author	Date	Statement	Reference
Gauzit	1941	At altitudes of 100 km and above nitrogen and oxygen must exist almost entirely in the atomic state	Compt. rend., 213, 695, (1941); Cahiers Phys., 9, 47, ('942); Bull. Am. Meteorol. Soc., 25, 245, (1944)
Bernard	1941	Estimated that the dissociation of N_2 is one-fifth at the base of the aurora and three-fourths at the upper limit	Phys. Rev., 55, 511, (1939); Ann. Astrophys., 4, 13, (1941)
Dufay	1943	At altitudes of the auroral light nitrogen must be entirely dissociated analogous to oxygen	Ann. Astrophys., 6, 81, (1943)
Deb	1952	1% dissociation at 90 km, 5% at 170 km, 25% at 400 km	J. Atm. Terrest. Phys., 2, 309, (1952)
Spitzer	1952	An appreciable fraction of nitrogen is atomic, at least at 300 km	The Atmospheres of the Earth and Planets, edited by G. P. Kuiper, The Univ. Chicago Press, pp. 217-219, (1952)
Sato	1953	Dissociation of nitrogen begins at the level of 120 - 130 km and proceeds to completion at about 180 to 220 km	J. Geomag. Geoelectr., 5, No. 3, 71, (1953)
A. P. Mitra	1954	To give adequate ionization for the F_1 region the ratio $n(N)/n(N_2)$ need not be larger than 1/10 at 200 km; 1/100 at 150 km	Indian J. Phys., 28, 269, (1954)

TABLE 9. STATEMENTS IN THE LITERATURE ABOUT THE VERTICAL DISTRIBUTION OF ATOMIC NITROGEN (Continued)

Author	Date	Statement	Reference
Nicolet	1954	Without doubt there is a real vertical distribution of atomic nitrogen, following Dalton's law, from 200 km to the exosphere	The Earth as a Planet, The Solar System, II, edited by G. P. Kuiper, The Univ. of Chicago Press, pp. 644-712 (1954)
Seaton	1955	The greater part of nitrogen may be in the atomic form at altitudes exceeding 300 km	The Air Glow and Aurorae, edited by E. P. Armstrong and A. Dalgarno, The Pergamon Press, London and New York, pp. 225-243, (1955)
Nicolet	1959	An exact determination of the vertical distribution of atomic nitrogen requires a knowledge of $n(N_2)$, $n(O)$, and $n(O_2)$ as well as the temperature. The maximum value of $n(N)$ should be obtained in the F_1 region and would be of the same order as that for $n(O_2)$ between 150 and 180 km under certain temperature conditions	Proc. I.R.E., <u>47</u>, 142, (1959)
Boyd	1959	Above 100 km oxygen is largely dissociated and above 300 km is probably more than ten times as abundant as atomic nitrogen	Nature, <u>183</u>, 361, (1959)

where J and K are rate coefficients, J being a function of height as given in the following expression

$$J = J_\alpha \exp(-\Sigma_k A_{k\lambda 1} n_k H_k \sec X)$$

$$J_\alpha = A(N_2) Q_\alpha \lambda$$

where Q_α is the number of photons at the relevant wavelength reaching the terrestrial atmosphere, A is the absorption coefficient for the constituent considered, and X is the solar zenith angle.

Calculations were made for two different nonequilibrium distributions of atomic nitrogen. For the first model the assumption was made that mixing predominates up to 150 km, with the ratio $n(N)/n(N_2)$ equal to 1/100 and this ratio increasing in value to 1/10 at 200 km. In the second model it was assumed that transition occurred between a narrow strip of 140-150 km with the concentration decreasing in accordance to its own scale height above 150 km.

For example the distribution followed the relationship

$$n(N) = n_{200}(N) \left[\frac{H}{H_o}\right]^{-\left[1+\frac{1}{\beta(N)}\right]}$$

where β (N) is the scale height gradient relevant to atomic nitrogen.

Figure 10 illustrates some early vertical distributions of atomic nitrogen. Figure 11 shows the distribution with altitude of atomic nitrogen along with other atmospheric components. It should be remarked that all of the distribution profiles will probably have to be revised when more data become available from planned rocket ascents and satellite flights.

1.13 THE LABORATORY PREPARATION OF ATOMIC NITROGEN

In the early experiments of Lord Rayleigh and others active

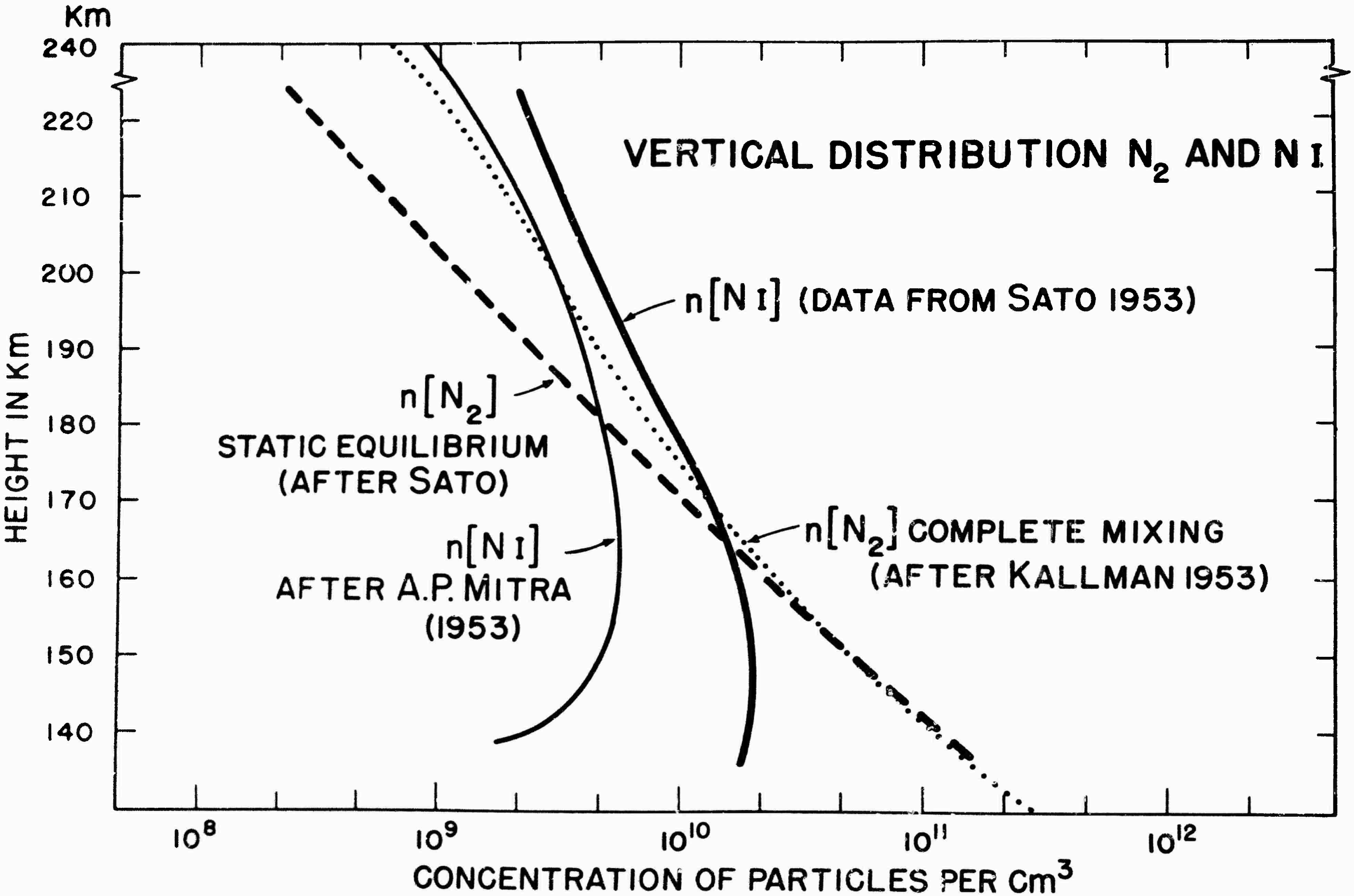


Fig. 10 SOME EARLY VERTICAL DISTRIBUTIONS OF ATOMIC NITROGEN

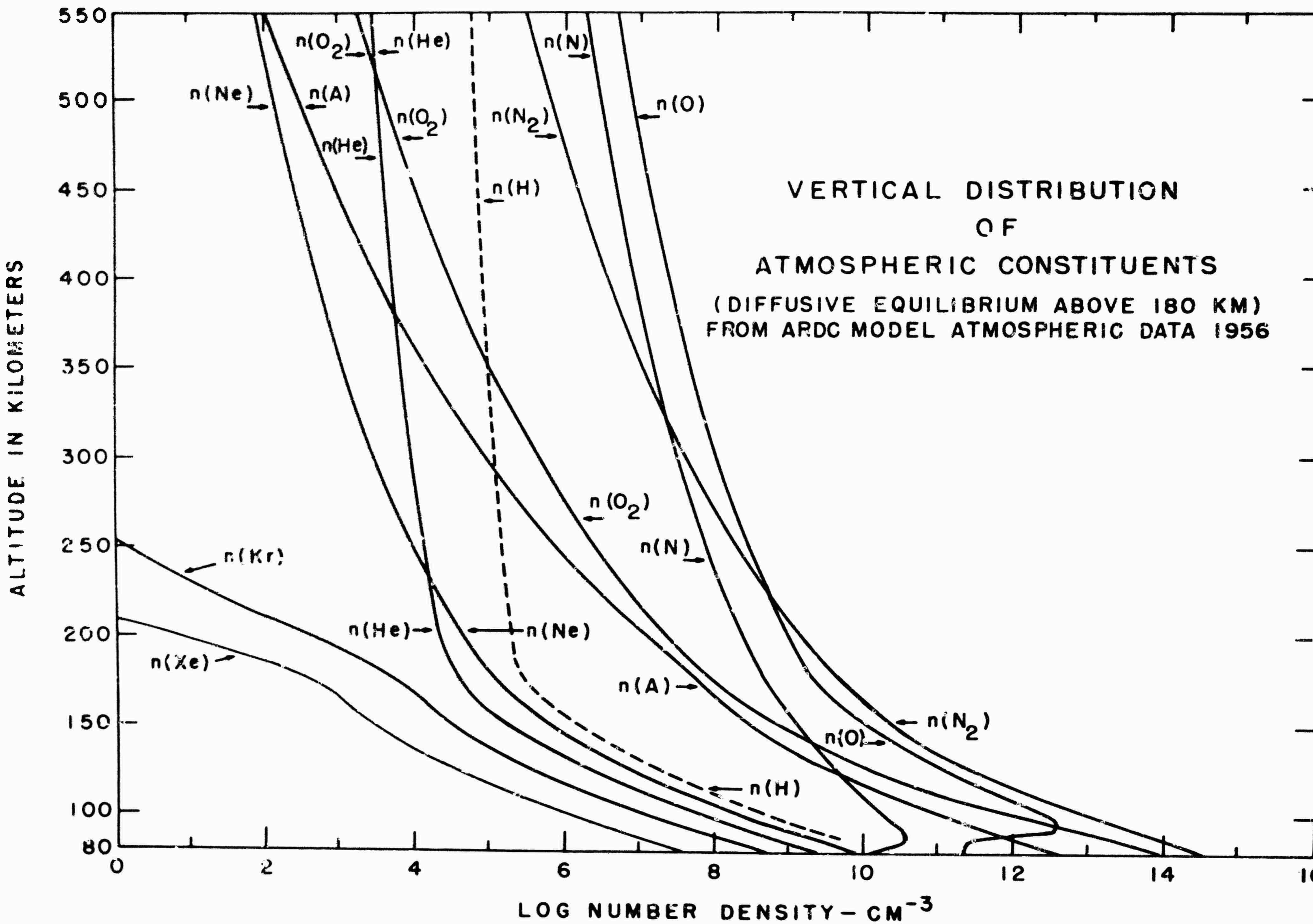


Fig. 11 THE AUTHOR'S DIAGRAM OF THE VERTICAL DISTRIBUTION OF N I ALONG WITH OTHER ATMOSPHERIC COMPONENTS.

nitrogen was produced by a condensed discharge in nitrogen at pressures of the order of 0.1 mm Hg. Later Rayleigh found that the electrodeless discharge was useful. However this method of production was limited to lower pressures and was less efficient. Stanley (1954) has described a high tension capillary arc source for preparation of active nitrogen. A high voltage a.c. arc was maintained in a quartz capillary tube between tungsten electrodes and was operated by a 250-volt a.c. supply through a transformer giving 5 to 10 kv and up to 500 ma. The current was calibrated by a variable resistance in the transformer primary circuit.

Kaufman and Kelso (1957) produced active nitrogen by an electrodeless microwave discharge (Raytheon Microtherm Model CMD-4) of 2400-mc frequency and about 50 to 100-w. microwave power output. Prepurified Matheson nitrogen was used. Kistiakowsky and Volpi also employed an electrodeless discharge operating on 2400 mc at 125-watt maximum output. Greenblatt and Winkler of McGill University produced nitrogen atoms by a high voltage condensed discharge. The electrical circuit consisted of a 4-mf condenser which was charged by a 3500-volt half-wave rectifier through a 20,000 to 50,000-ohm resistance. The discharge tube was a pyrex tube with a length of 70 mm and a 20-mm inside diameter. Aluminum foil electrodes were used.

Broida and Pellam have described in U.S. Patent 2,892,766, June 30, 1959, the method for preparation of nitrogen atoms and free radicals employed at the U. S. National Bureau of Standards. Nitrogen gas at a pressure of 0.1 to 10 mm Hg is exposed to an electrodeless discharge excited by a microwave voltage (2450 mc/sec). The atoms and radicals produced are condensed in a trap which is maintained at a temperature of 4.2°K by a liquid helium bath.

1.14 LABORATORY METHODS FOR THE QUANTITATIVE MEASUREMENT OF ATOMIC NITROGEN

Spealman and Rodebush (1935) measured the percentage of dissociation of nitrogen by a Wrede gage which is described by Rodebush and Klingelhoefer [J. Am. Chem. Soc., 55, 130, (1933)]. The Wrede gage [Z. Physik, 54, 51, (1929)] is a diffusion gage consisting of an orifice 0.1 mm in diameter and of gages for measuring the total and differential pressures. The orifice is constructed in a thin glass film sealed on the end of a 5-mm tube which extended into the gas stream at a point about 7 centimeters from the discharge tube. Greenblatt and Winkler (1949) also used a Wrede gage for measuring the nitrogen atom concentration. The gage consisted of a porous disk which was used as a diffusion orifice; the pressure differential across the orifice was measured with McLeod gages.

More recently a pseudo-titration process using nitric oxide (NO) has been found to be a convenient and accurate method for determining the concentration of atomic nitrogen. The method has been described and used by Harteck, Reeves, and Mannella (1958) in determining the rate of recombination of nitrogen atoms. Kaufman and Kelso (1957) and Kistiakowsky and Volpi (1957) have studied the reaction of atomic nitrogen with nitric oxide. The reaction of nitrogen atoms with NO

$$N + NO \xrightarrow{k_1} N_2 + O$$

is essentially instantaneous. The rate of the reaction has been determined by Kistiakowsky and Volpi to be $k_1 \geq 4 \times 10^{11}$ cm^3 mole^{-1} sec^{-1}

or 6.6×10^{-13} cm^3 sec^{-1}.

As the NO is added into the system through a calibrated leak from zero to an equimolecular amount of atomic nitrogen, the afterglow changes from the st raw-yellow (Lewis-Rayleigh afterglow) of pure atomic nitrogen to the blue-glow of NO which disappears at the end point. The characteristic blue color is the result of the γ, β, and δ bands of NO because of the following reactions:

$$N + O + M \longrightarrow NO\ (A\ {}^2\Sigma^+,\ B\ {}^2\Pi) + M$$

$$NO\ (A\ {}^2\Sigma^+,\ B\ {}^2\Pi) \longrightarrow NO + h\nu\ (\gamma,\ \beta \text{ and } \delta \text{ bands})$$

At the end point when the N atoms are consumed, the atomic oxygen atoms formed in the titration react with the excess NO according to the reaction

$$NO + O \xrightarrow{k_2} NO_2 + h\nu \quad \text{(continuum)}$$

which produces a pale green or whitish afterglow. Kaufman gives a value for k_2 in this reaction of

$$k_2 \geq 1.5 \times 10^7 \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$$

$$\text{or } 2.5 \times 10^{-17} \text{ cm}^3 \text{ sec}^{-1}$$

Reference: Proc. Roy. Soc., <u>A247</u>, 123, (1958).

At the point where the whitish or greenish glow fades and the blue glow appears, the NO leaking into the system is equal to the concentration of nitrogen atoms. The latter concentration is obtained by reading the pressure of the NO and calculating the flow.

1.15 SUMMARY AND INTERPRETATION

In the past the making of a survey and appraisal of the current state of knowledge in the geophysics of the upper atmosphere, as well as in the basic sciences such as chemistry and physics, has demonstrated its usefulness in pointing out the direction and nature for future research. Up to the present time there have been many observations on the luminescence of the night sky and auroral spectra. In regard to atomic nitrogen its presence appears to have been established. With improvements in new spectrographic equipment a larger number of weak atomic lines of nitrogen and oxygen appear to be present which heretofore were considered to be absent.

There is disagreement about the height of the luminescence, the intensity, and the amount of the constituents which contribute to the night airglow and auroras. Even less clear is the mechanism of vertical distribution and the quantity of the atmospheric species present at various altitudes. A few rocket flights have yielded meager data about the distribution and amount of atomic oxygen to altitudes of about 100 to 200 km. As yet there are no experimental data about the vertical distribution and quantity of atomic nitrogen at high altitudes.

Numerous rocket and satellite flights have attempted to determine the density of the upper atmosphere at different altitudes. There is no definite temperature profile with altitude except those based upon certain assumptions made in regard to molecular weights. Many inconsistencies exist in regard to the density and pressure of the atmosphere at high altitudes, both of which are dependent upon the quantities of atmospheric gases present. It might be concluded that until we know definitely the amount and vertical distribution of these gases, and the factors which influence them, our knowledge of the upper atmosphere will remain incomplete and very limited.

APPENDIX I

TABLE OF PHYSICO-CHEMICAL CONSTANTS

(Based on Cohen, Du Mond, Layton, and Rollett
Rev. Mod. Phys., 27, 363, [1955])

(CHEMISTS SCALE)

I Values of the Basic Constants

Velocity of light in vacuo $\quad c = 2.99793 \times 10^{10}$ cm sec^{-1}

Planck's constant $\quad h = 6.62517 \times 10^{-27}$ erg sec

Avogadro's number $\quad N = 6.02322 \times 10^{23}$ molecules mole^{-1}

Faraday constant* $\quad F = 96,489.9 \ (\pm 2.0)$ coulombs/gm equivalent
(on chemical scale)

$= 96,516.4 \ (\pm 2.0)$ coulombs/gm equivalent
(on physical scale)

Conversion factor chemical to physical 1.000275

*Reference: Tech. News Bull. Bur, Standards, 44, 34-35, (1960)

Ice point, 0°C $= 273.15^\circ$K

Pressure-Volume product for 1 mole of a gas at 0°C and 1 atmosphere pressure $\quad pV = 22,414.6$ cm^3 atm mole^{-1}

II Values of the Derived Constants

Electronic charge $\quad e = \frac{F}{N} = 1.60206 \times 10^{-19}$ abs. coulomb
1.60206×10^{-20} emu
4.80286×10^{-10} esu

Electron volt $\quad$ ev $= 1.60206 \times 10^{-12}$ erg

ev $= 23.063$ kcal mole^{-1} $= 23,063$ cal mole^{-1}

ev $= 1 \times 10^{-6}$ mev

Gas constant $R = 8.31470 \times 10^{7}$ erg mole^{-1} degree^{-1}

8.31470 joules mole^{-1} degree^{-1}

1.9873 cal mole^{-1} degree^{-1}

82.05667 cm^{3}-atm mole^{-1} degree^{-1}

Boltzmann constant $K = \frac{R}{N} = 1.38044 \times 10^{-16}$ erg degree^{-1}

Loschmidt s number $n_o = \frac{N}{2.24146 \times 10^{4}\ \mathrm{cm}^{3}} = 2.68717 \times 10^{19}$ cm^{-3}

Wavelength of 1 ev quantum = 12,397.67 A

Wave number of 1 ev quantum = 8,066.03 cm^{-1}

Temperature associated with 1 ev (F/R) $10^{8} = 1.16052 \times 10^{4}$ °K

III Values of the Defined Constants

Acceleration of gravity (standard) g = 980.665 cm sec^{-2}

Atmosphere (standard) atm = 1.01325×10^{6} dynes cm^{-2}

Standard millimeter of mercury pressure mm Hg = 1/760 atm

IV Values of Certain Auxiliary Relationships

1 micron $1\mu = 0.001\ (10^{-3})$ mm $= 10^{4}$ A

1 millimicron $1\mathrm{m}\mu = 10^{-6}$ mm = 10 A

1 Angstrom 1 A = 10^{-8} cm = 10^{-7} mm

1 A = 10^{-1} mμ = $10^{-4}\mu$

1 liter = 1,000.028 cm^{3}

The quantum yield $\Phi = \dfrac{\text{Number of molecules reacting chemically}}{\text{Number of quanta absorbed}}$

An energy unit which is used frequently in photochemistry as well as nuclear chemistry is the electron volt (ev). It is the energy acquired by an electron in falling through a potential difference of 1 volt. Since the charge of the electron is 1.60206×10^{-19} coulomb, this energy is

$$
\begin{aligned}
1 \text{ ev} &= 1.60206 \times 10^{-19} \text{ coulomb} \times 1 \text{ volt} \\
& 1.60206 \times 10^{-19} \text{ volt-coulomb or joule} \\
& 1.60206 \times 10^{-12} \text{ erg}
\end{aligned}
$$

The energy associated with the Avogadro number of electrons each accelerated by a 1-volt potential is

$$
1 \text{ ev} = \frac{(1.60206 \times 10^{-19} \text{ joule electron}^{-1})(6.02322 \times 10^{23} \text{ electrons mole}^{-1})}{4.1840 \text{ joule cal}^{-1}}
$$

$$
1 \text{ ev} = 23{,}063 \text{ cal mole}^{-1} = 23.063 \text{ kcal mole}^{-1}
$$

Other units commonly used as a measure of energy-level spacings in potential energy diagrams are the temperature T and the wave number $\bar{v}$ in cm^{-1}. Since $E = h\nu = hc/\lambda = hc\bar{v} = KT$, it is obvious that $\bar{v}$ is just equal to the number of waves per centimeter. These two units are related to the electron-volt by the following numerical factors:

$$
\begin{aligned}
1 \text{ ev} &= 8.06603 \times 10^{3} \text{ cm}^{-1} \\
1 \text{ cm}^{-1} &= 1.44 \text{ deg. K}
\end{aligned}
$$

The fact that the cm^{-1} is of the same order as the degree is very useful in making quick calculations to determine which energy levels will be populated at any given temperature.

The temperature associated with one electron-volt is found through the relationship: Faraday's constant/Universal Gas constant (Faraday constant $= \frac{Ne}{c}$ where N is the Avogadro number, e the electronic change, and c is the velocity of light).

Conversion Factors for Units of Molecular Energy

Multiply by appropriate entry to obtain →	ev mole^{-1}	erg mole^{-1}	kcal mole^{-1}	cal mole^{-1}	joule (abs) mole^{-1}	A mole^{-1}	cm^{-1} mole
1 ev mole^{-1}	1	1.60206×10^{-12}	23.063	23,063	96,495.6	12,397.67	8066.03
1 erg mole^{-1}	6.24196×10^{11}	1	1.43958×10^{13}	1.43958×10^{16}	6.02322×10^{16}	7.7386×10^{15}	5.03478×10^{15}
1 kcal mole^{-1}	4.33595×10^{-2}	6.9464×10^{-14}	1	1×10^{3}	4184.0	5.3322×10^{2}	3.4973×10^{2}
1 cal mole^{-1}	4.33595×10^{-5}	6.9464×10^{-17}	1×10^{-3}	1	4.1840	0.53321	0.34973
1 joule (abs) mole^{-1}	1.03524×10^{-5}	1.66024×10^{-17}	2.39006×10^{-4}	0.239006	1	0.12848	8.3589×10^{-2}
1 A mole^{-1}	8.06603×10^{-5}	1.29223×10^{-16}	1.86027×10^{-3}	1.86027	7.7833	1	0.650608
1 cm^{-1} mole^{-1}	1.239767	1.98618×10^{-16}	2.85927×10^{-3}	2.85927	11.9632	1.53702	1

Energies for Various Spectral Regions and Wavelengths

Spectral Region	Wave-length A	Wavelength cm	Wave Number $\bar{\nu}$ cm^{-1}	Frequency ν	Energy of 1 quantum $h\nu$ ergs	Electron volts
Far infrared	1,000,000	10^{-2}	10^{2}	3×10^{12}	1.99×10^{-14}	0.01
Infrared	100,000	10^{-3}	10^{3}	3×10^{13}	1.99×10^{-13}	0.12
Near infrared	10,000	10^{-4}	10^{4}	3×10^{14}	1.99×10^{-12}	1.25
Edge of visible	8,000	8×10^{-5}	1.25×10^{4}	3.75×10^{14}	2.48×10^{-12}	1.55
Edge of visible	4,000	4×10^{-5}	2.50×10^{4}	7.5×10^{14}	4.97×10^{-12}	3.10
Ultra violet	2,000	2×10^{-5}	5.00×10^{4}	1.5×10^{15}	9.93×10^{-12}	6.20
Ultraviolet	1,000	1×10^{-5}	1×10^{5}	3×10^{15}	1.99×10^{-11}	12.40
X rays	1	1×10^{-8}	1×10^{8}	3×10^{18}	1.99×10^{-8}	12,400
X rays	0.1	1×10^{-9}	1×10^{9}	3×10^{19}	1.99×10^{-7}	124,000
X rays	0.01	1×10^{-10}	1×10^{10}	3×10^{20}	1.99×10^{-6}	1.24×10^{6}

2. SUMMARIES OF ABSTRACTS AND PAPERS

1900

Lewis, Percival, "Some New Fluorescence and Afterglow Phenomena in Vacuum Tubes Containing Nitrogen", Astrophys. J., 12, 8, (1900)

The author reported that while investigating the effects of impurities on the spectrum of nitrogen he observed a peculiar fluorescent and afterglow effect. This appeared to be due to the presence of exceedingly small traces of oxygen or water vapor. The fluorescence which Lewis termed " β-flurescence" was not limited to the path of the discharge and was really fluorescence of the gas, not direct radiation from the gas.

It was observed that when the nitrogen was free from traces of oxygen the fluorescence was considerably weaker. The ultraviolet region was photographed. It was concluded from this investigation of the ultraviolet that a temporary emission of powerful ultraviolet radiation accounted for the β -fluorescence. Reference was made to the studies of Deslandres [Compt. rend. 101, 1256, (1885)] which appeared closely related to those observed by Lewis.

Reference was also made to Morren [Ann Chim. Phys. 4, 293, (1865)], Sarasin [Pogg. Ann. 140, 425, (1870)], and Warburg [Arch. de Gen. (3), 12, 504, (1884)]. J. J. Thomson [Phil. Mag. 32, 335, (1891)] used electrodeless tubes and found an afterglow in air with a spectrum composed of lines or bands. From a careful investigation of the afterglow in nitrogen, Lewis in the present paper showed that the phenomenon depended on the presence of small traces of water vapor or oxygen. The author also observed that the afterglow was produced only with condenser and spark gap and that the spectrum was banded, not continuous.

1903

Schumann, Victor, "On the Absorption and Emission of Air and Its Ingredients for Light of Wavelengths from 250 $\mu\mu$ to 100$\mu\mu$."

Smithsonian Contributions, (A Part of Volume XXIX), No. 1413, (1903).

In the present report Dr. Schumann has described the most essential results obtained up to the end of the year 1900. The instrument employed in this investigation was a vacuum-spectrograph with lenses and prism of white fluor-spar. A detailed description of the instrumentation is included along with nine photographic reproductions of the author's original working drawings of the apparatus constructed by the author.

The experimental methods of filling the Geissler absorption and emission tubes, the preparation of the ultraviolet photographic plates, and the difficulties to be avoided are fully discussed. The source of light for the absorption experiments was a Geissler tube of hydrogen closed with a fluor-spar window. The pressure in the absorption tubes was equal to atmospheric pressure at the time, while the pressure in the emission tubes varied from 0.05 to 1 centimeter of mercury pressure. The electric discharge was effected either by a Ruhmkorff coil alone, or with a Leyden jar, or a Leyden jar and interposed spark gap in the circuit. The primary current did not exceed 2.5 amperes and 10.5 volts.

The author observed that nitrogen proved very transparent even beyond 162 $\mu\mu$ but nevertheless absorbed particular wavelengths very energetically. The emission bands of nitrogen consisted of a number of groups of bands of moderate photographic power diminishing toward the shorter wavelengths. Beyond 185 $\mu\mu$ the author was unable to detect any nitrogen bands.

Lewis, Percival, "Afterglow of Metallic Vapors in Nitrogen", Astrophys. J., 20, 49-57, (1904).

The author describes the continuation of his investigation of the spectrum of the afterglow in nitrogen. There is the possibility of traces of NO contained in the purified nitrogen used during these investigations. He points out that the afterglow could only be obtained with a strong condenser discharge. The spectrum is discontinuous and consists of lines and bands. Lewis observes that there is no afterglow of the metallic vapors when there is no afterglow in the gas.

Lewis, Percival, "The Spectrum of the Electrodeless Discharge in Nitrogen", Phys. Rev., 18, 124-125, (1904).

This is an abstract of a paper presented before the 22nd Meeting of the American Physical Society held 30 December 1903 in St. Louis, Missouri. Some preliminary observations are reported of the spectrum of the electrodeless discharge in nitrogen. A spherical glass bulb with a quartz window was employed. The paste-board cylinder which surrounds the bulb was wound with eight turns of copper wire in circuit with a spark gap and condenser.

The spectrum was photographed. The second group of bands appeared strong. The negative bands appeared on all the plates although they were weak in comparison with the positive bands.

Lewis, Percival, "The Spectrum of the Afterglow of the Spark Discharge in Nitrogen at Low Pressures", Phys. Rev., 18, 125-128, (1904).

An afterglow which appeared different from those previously observed both in origin and spectrum was noted by the author in 1899 and reported in 1900 [Ann Physik 2, 459,(1900), Astrophys. J. 12, 8,(1900), and

ibid., 20, 50, (1904)]. The afterglow was produced in nitrogen as pure as could be produced. It is stated that infinitesimal traces of oxygen might be necessary, but perceptible traces would destroy it. The appearance of the glow was described as a rich chamois yellow fog, extending several inches into the connecting tubes and persisting for several seconds after the discharge had ceased.

When platinum electrodes were substituted for aluminum electrodes both the afterglow and the visible spectrum remained unchanged. The author suggested that he planned to investigate whether the phosphorescence was possible in absolutely pure nitrogen, or if the presence of any foreign substance was necessary.

1911

Fowler, A., and R. J. Strutt, "Spectroscopic Investigations in Connection with the Active Modification of Nitrogen. I. Spectrum of the Afterglow", Proc. Roy. Soc. (London), A 85, 377, (1911).

The spectrum observed in this investigation was considered to consist of three groups of bands. In group α the brightest bands were found to occur at about wavelengths 6252, 5804, and 5407 A. Another weaker band was observed at 5054 A. In group β a series of eleven bands in the violet and ultraviolet were found in the region 4312 to 2503 A. Group γ corresponded with Deslandres' "third positive" group of nitrogen bands. Each of the groups are described in detail. The third group of afterglow bands appeared to be identical with the third positive group of nitrogen bands previously reported by Lewis (1900).

Lyman, Thedore, "The Spectra of Some Gases in the Schumann Region", Astrophys. J., 33, 98, (1911).

The results are given of an investigation on the nature of the radiation from O_2, H_2, N_2, He, and A in the short wavelength (1900 to 1300 A) region. The vacuum spectroscope devised by Lyman was used. A detailed description of the apparatus and experimental method is given.

With reference to nitrogen, this gas was prepared from a mixture of NH_4Cl. $NaNO_2$, and $K_2Cr_2O_7$ dissolved in water. The gas was purified by passage over KOH, through concentrated H_2SO_4, over P_2O_5, and finally over hot metallic copper. The gas pressure of 2 mm was selected. A table is included which gives the wavelengths of the band system (1383.7 to 1870.9 A) and the line spectrum (1492.7 to 1745.3A) for nitrogen.

Strutt, R. J. (later Lord Rayleigh) "A Chemically Active Modification of Nitrogen, Produced by the Electric Discharge. I.", Proc. Roy. Soc. (London), A 85, 219, (1911).

In the Bakerian Lecture given 6 April 1911 the author of the present paper referred to the work of Lewis [Ann. Phys. 2, 466, (1900)]. The following effects were studied: (a) effect of temperature, (b) effect of an electric field, (c) the action of the after-glowing nitrogen on the non-metals, (d) the action on the metals and production of metallic line spectra, and (e) the action on chemical compounds.

It was established that pure nitrogen, regardless of the source, when subjected to the jar discharge undergoes some modification which causes it to glow for a short time after it has left the discharge. The modified nitrogen was shown to be very reactive chemically, combining

with phosphorus, metallic sodium, heated mercury, nitric oxide, acetylene, halogen derivatives of organic radicals, and several other non-metals and chemical compounds.

Strutt, R. J. (later Lord Rayleigh) "A Chemically Active Modification of Nitrogen, Produced by the Electric Discharge. II.", Proc. Roy. Soc. (London), A 86, 56, (1911).

This is a continuation of the Bakerian Lecture for 1911 [Proc. Roy. Soc. A 85, 219, (1911)]. The paper describes the action of active nitrogen on (a) nitric oxide, (b) nitrogen dioxide, (c) phosphorus, (d) the electrical properties of glowing nitrogen, and (e) attempts at condensation.

A brief summary is included. The author was unable to isolate the active nitrogen by liquid air condensation. Oxygen was reported to destroy the active nitrogen, but did not combine with it.

1912

Strutt, R. J. (later Lord Rayleigh) "A Chemically Active Modification of Nitrogen, Produced by the Electric Discharge. III.", Proc. Roy. Soc. (London), A 86, 262, (1912).

This paper describes further experiments and observations upon the active modification of nitrogen. The effect of temperature on the duration of active nitrogen was studied. A sealed tube containing nitrogen at low pressure was excited by the electrodeless discharge; when allowed to stand at room temperature the glow in the tube was conspicuous for a minute of more. If the bulb was immersed in liquid air immediately after excitation, the glow was very brilliant when viewed under the surface of the liquid air. This indicated that the active

nitrogen emitted its energy more readily at low temperatures.

The effect of compressing the gas was also studied. The observation that the glowing gas under pressure flashed out with great brilliance lead the author to suggest that the glow-transformation was polymolecular.

Strutt, R. J. (later Lord Rayleigh) "A Chemically Active Modification of Nitrogen, Produced by Electric Discharge. IV ", Proc. Roy. Soc. (London), A 87, 179, (1912).

This investigation had for its purpose the study of the energy of active nitrogen, the ionization attendant on the decay of the gas, and the effect of temperature. Active nitrogen was shown to be a highly endothermic body, with its energy of the same order of magnitude as that of other chemical substances. In reverting to ordinary nitrogen the number of atoms ionized was shown to be only a very small fraction of the whole number involved in the change. The ionization was suggested to be due to light of very short wavelength emitted in the reaction. Additional experiments on the effect of temperature showed that the change of active nitrogen to ordinary nitrogen was more rapid at low temperature. This was interpreted to be connected with the monatomic character of the molecule.

1913

Comte, F., "Chemically Active Modification of Nitrogen", Z. Physik, 14, 74-76, (1913).

The author states that the phenomeno observed by Strutt (1913) and ascribed to an active form of nitrogen was found to be due to traces of oxygen in the nitrogen. Comte suggested that traces of oxygen could be best removed with glowing copper. The formation of a cloud in the phosphorus pipet was given as a very delicate test for traces of oxygen when purification with phosphorus was employed.

Koenig, A., and E. Elöd, "The Afterglow in Pure Nitrogen Following the Passage of Electrical Discharge", Z. Physik, 14, 165, (1913).

The results of the experiments by Koenig and Elod appeared to indicate the original theory of Stratt. It was reported that instead of becoming less intense with successive purification of the nitrogen by removing foreign gas, the afterglow became stronger and longer lived.

Lewis, E. Percival, "The Origin of the Bands in the Spectrum of Active Nitrogen", Phil. Mag., [6], 25, 826-832, (1913).

Reference is made to the controversy of whether the afterglow occurs only in nitrogen entirely free from oxygen. The author reports that while studying the spectra of mixtures of nitrogen and oxygen the third group of nitrogen bands could be obtained when approximately pure nitrogen was used, but when a small quantity of oxygen was added they invariably appeared. Thus the study of the nitrogen afterglow was restudied by the author. The following results are reported:

a. The ture afterglow spectrum of nitrogen containing a trace of oxygen initially: after the afterglow was established, oxygen was added to raise the pressure 15 percent; the third and β groups appeared strong but the second positive group did not appear. b. The condensed discharge in the same gas (taken before a): the fourth group of bands did not appear. c. The condensed discharge in nitrogen containing a small trace of oxygen: the β group was clearly observed. d. The true afterglow spectrum with a minimum of oxygen present: the third group and β group were absolutely lacking.

Strutt, R. J. (later Lord Rayleigh) "An Active Modification of Nitrogen, Produced by the Electric Discharge. V.", Proc. Roy. Soc. (London), A 88, 539, (1913).

In the fifth paper in the series on active nitrogen, the author made reference to Comte [Phys. Z. 14, 74, (1913)] and to Tiede [Ber. Chem. Gesell. 46, 340, (1913)] who had repeated the experiments of Strutt. These workers had reported that they did not obtain the phenomena of active nitrogen in the absence of traces of oxygen. Reference was made also to Koenig and Elöd [Phys. Z. 14, 165, (1913)] who confirmed the original conclusion of Strutt that nitrogen alone is concerned in the observed phenomena in active nitrogen.

In the present paper an improved practical method of preparing and storing nitrogen for the experiments is described. The author concluded, notwithstanding the criticisms from other experimenters, that the presence of traces of oxygen in the nitrogen was not essential or even favorable to the phenomena.

Further experiments upon the reaction of active nitrogen with the vapor of mercury, cadmium, zinc, arsenic, sodium, and sulfur were included in the study. In all cases the reaction with these elements yielded the nitrides. Also the reaction with carbon disulfide, chloride of sulfur, and organic compounds was studied. There did not appear to be any definite connection with the development of spectra by active nitrogen and the chemical reactions in progress.

1914

Baker, H. B., Erich Tiede, R. J. Strutt, and Emil Domcke, "Active Nitrogen", Nature, 93, 478, (1914).

In view of the apparently inexplicable contradictions between

the results of Tiede and Domcke reported in Ber. 46, 801, 4095, (1913) and those of Baker and Strutt reported in Ber. 47, 801 and 1049, (1914), it was arranged that each pair of investigators in the presence of the other should repeat their experiments. As a result of these joint experiments it was concluded that the addition of a trace of oxygen to the nitrogen sample caused the glow to appear more easily and with increased intensity.

It was considered possible that the effect of the infinitesimal trace of oxygen was to change the condition of discharge so as to make it more suitable for the production of active nitrogen. Reference was made to Warburg's observations on the effect of traces of oxygen on the fall of potential of nitrogen which tended to confirm this idea. It was suggested that possibly substances other than oxygen could be found to produce the same effects.

Baker, H. B., Erich Tiede, R. J. Strutt, and Emil Domcke,
"Active Nitrogen",
Ber., 47, 2283, (1914).

This is a report of the joint experiments by the authors on the formation of active nitrogen catalyzed by 0.1 per cent of oxygen. The same report was published in Nature 93, 478, (1914). The summary is given under the latter reference.

1915

Strutt, R. J. (later Lord Rayleigh), "A Chemically Active Modification of Nitrogen, Produced by the Electric Discharge. VI.," Proc. Roy. Soc. (London), A 91, 303, (1915).

The author has previously given a review of the past controversy as to whether active nitrogen can be freely obtained from pure nitrogen, or

whether a trace of oxygen must be present. In the present paper the effect of various catalysts in promoting the formation of active nitrogen is reported. It is concluded that minute traces of any foreign gas will enormously increase the yield of active nitrogen.

The most effective catalysts are listed as H_2S, O_2, H_2O-vapor Hg-vapor, CO_2, Cl_2, CO, C_2H_2, C_2H_4, CH_4, and H_2. Argon, helium, and nitrogen itself were unable to promote the formation of active nitrogen. Further chemical reactivity of active nitrogen is reported.

1916

Strutt, R. J. (later Lord Rayleigh), "An Active Modification of Nitrogen. VII.", Proc. Roy. Soc. (London), A 92, 438, (1916).

In the previous papers of this series the author has emphasized the properties of active nitrogen when produced. The present paper is concerned with the circumstances of the production of active nitrogen by the electric discharge. Some of the factors studied were the following.

a. Various regions in the luminous discharge.

b. Wide discharge tubes compared with narrow.

c. Effect of varying the discharge length traversed. Destruction of active nitrogen in the discharge.

d. Traces of oxygen affect the afterglow profoundly. Do they simultaneously affect the discharge potential?

e. Active nitrogen at atmospheric pressure.

f. Scattered metal from the cathode in a stream of active nitrogen.

One of the conclusions reached was that production of active nitrogen is greatest near the cathode. If falls off to a minimum in the Faraday dark space and increase again in the positive column to a constant value which is less than at the cathode. The yield of active nitrogen

reaches a limit as the length of the positive column traversed is increased. While a trace of oxygen greatly increases the yield of active nitrogen, it also increases the fall of potential at the cathode. When active nitrogen is produced by the spark at atmospheric pressure the phenomena is much less striking than at low pressures.

1917

Strutt, R. J. (later Lord Rayleigh), "Spectroscopic Observations on the Active Modifications of Nitrogen. V.", Proc. Roy. Soc. (London), A 93, 254, (1917).

This is the fifth paper in the series upon the spectroscopic observations on the active modification of nitrogen. The previous papers in the series occur in Proc. Roy. Soc. (London) I, A 85, 377, (1911); II, A 86, 105, (1911); III, A 89, 187, (1913); and IV, A 91, 120, (1915).

It was established that the faint red bands 6394.45, 6468.53, 6544.81 and 6623.52 A belonging to the first positive group truly belong to the afterglow of nitrogen. The second positive group is reported to be entirely absent from the afterglow spectrum. The β and γ groups appear only when oxygen-containing gases are introduced into the afterglow. When oxygen is introduced into the afterglow there appeared to be no detectable oxidation of nitrogen.

1923

Pirani, M. and E. Lax, "Observations on the Afterglow of Active Nitrogen", Wiss. Veroffentl. Siemens - Konzern 2; 203-208, (1922), C. A., 17, 2676, (1923).

On the basis of experiments on the discharge through nitrogen con-

tained in a two-liter vessel of a current of frequency about 100,000 cycles per sec., the authors attributed the afterglow of active nitrogen to the presence of minute traces of impurities, particularly electronegative gases and vapors such as oxygen, water vapor, and iodine. Rare gases and electropositive gases such as hydrogen exerted very little influence upon the phenomenon, which was not exhibited by absolutely pure nitrogen. The phenomenon was attributed to the conversion of the nitrogen into an active modification, which is destroyed with the emission of light in the presence of electronegative gases.

Lewis, E. P., "Phosphorescence Caused by Active Nitrogen", Nature, 111, 599-600, (1923).

The author reports that active nitrogen excited phosphorescence in a number of solid salts. Among those reported are $UO_2(NO_3)_2$, ZnS, $BaCl_2$, $SrCl_2$, CsCl, LiCl, NaCl, Kcl, NaI, KI, Na_2CO_3, $SrBr_2$. The spectra appeared to be continuous except in the case of uranium salts which showed characteristic bands. It is suggested that the phoenomenon is due to chemical reactions with active nitrogen.

It was found that the afterglow depended on the presence of a trace of oxygen or some other electronegative element and is destroyed by more than a trace. The author suggests that NO is formed with an excess of oxygen and that this caused the emission of Deslandres' third group of bands.

Lewis, E. P. "Phosphorescence Caused by Active Nitrogen", Phys. Rev., 21, 713, (1923).

This is an abstract of a paper presented at the 120th regular meeting of the American Physical Society held at the Bureau of Standards, 20-21 April 1923. Reference is made to the author's paper in the Astrophysical

Journal 20, 49, (1904) in which he first described the spectrum of the afterglow of active nitrogen. In the present paper a number of compounds are reported to phosphoresce in the present of active nitrogen.

The presence of free electrons in active nitrogen was considered to be the cause of its properties. This was indicated by the fact that when active nitrogen streams by an insulated electrode, positive but not negative electricity is discharged.

Vegard, Lars, "The Auroral Spectrum and the Upper Strata of the Atmosphere", Phil. Mag., [6], 46, 193, (1923).

This is an excellent paper describing the composition of the upper atmosphere as it was known in 1923. Vegard states that during the winter of 1921 at Christiania he had made determinations of the green auroral line and found it to have a wavelength of 5578.0 A. He remarks that the origin of the line remained as mysterious as ever. He also mentions that during the winter of 1922-1923 three spectrographs had been installed for his disposal at the Geophysical Institute of Tromso.

The auroral line λ3467.8 A is recorded in Table 1 of the paper together with the values of wavelengths determined for a considerable number of other lines in the auroral spectrum. The lines were interpreted as partly belonging to the negative and partly to the positive band spectrum of nitrogen.

This paper is of great historical interest since Vegard considers the question of a hydrogen and helium atmosphere above an altitude of about 100 km. He concludes that the hydrogen and helium layer which had earlier been supposed to dominate at the top of the atmosphere does not exist. He discusses the question of the existence of some light unknown gas, geocoronium, and thinks that the occurrence of this new gas is very unlikely. Vegard ascribes the green line (5578 A) to nitrogen and

considers nitrogen to predominate up to the very limit of the atmosphere.

1924

McLennan, J. C. and G. M. Shrum, "On the Luminescence of Nitrogen, Argon, and other Condensed Gases at Very Low Temperatures", Proc. Roy. Soc. (London), A 106, 138-149, (1924).

The authors state that one of the outstanding problems awaiting solution in the field of spectroscopy is the origin of the famous green line, λ 5577 A, in the spectrum of the auroral light. The authors conclude from their experiments that the excited luminescence lines in the spectra of very cold nitrogen and argon did not coincide even in part with the green auroral line λ 5577 A.

Reference is made to investigations by Vegard and Kammerlingh Onnes who concluded that the auroral green line λ 5577A had its origin in radiations from suspended solid nitrogen. McLennan and Shrum could not verify this conclusion from their experiments. A plate of photographs is included showing the analysis of the light of the luminescence of solid nitrogen. The experimental methods are described in detail.

Vegard, L., "The Auroral Spectrum and the Upper Atmospheres", Nature, 113, 716-717, (1924).

Professor Vegard states that he first began observations on the auroral spectrum at Bossekop in Finmarken in 1912-13. The prominent green line at λ 5577 A was observed and interpreted to be identical with prominent lines in the negative band spectrum of nitrogen. Vegard gives an account of his experiments at the Kammerlingh Onnes Cryogenic Laboratory of Leyden where he bombarded solid nitrogen with

cathode rays. The green auroral line at λ 5577 A observed in the luminescence from these experiments were considered to be identical to the λ 5577 A line in the auroral spectrum.

Vegard, L., "The Light Emitted from Solid Gases and its Relations to Cosmic Phenomena", Nature, 114, 357-359, (1924).

This paper gives an account of Vegard's experiments at the Cryogenic Laboratory of Leyden. The relative intensity of the lines N_1 and N_2 in the band system of nitrogen was studied in relation to the importance to the auroral spectrum. Layers of solid oxygen, ammonia, argon, and nitroys oxide were also bombarded with cathode and canal rays. These gases gave no afterglow except for argon which gave a weak one. The afterglow of nitrogen at temperatures below $35.5^{\circ}K$ was considered unique and singular in its application to the auroral spectrum.

1925

Birge, R. T. and J. J. Hopfield, "The Quantum Analysis of New Nitrogen Bands in the Ultraviolet", Nature, 116, 15, (1925).

In this letter to the editor of Nature the authors report their measurements and analysis of a new group of nitrogen bands with an origin at about 65,000 ν . The spectral region extended from λ 1354 to λ 1854 A. There are many other bands between λ 950 and λ 1350 A, some of which were reported to be quite strong. Also a number of weak bands between λ 1350 and λ 2100 A, but without consistent numerical relations, are reported.

Hopfield, J. J. and R. T. Birge, "The Quantum Analysis of New Nitrogen Bands in the Ultraviolet", Phys. Rev., 26, 283, (1925).

In this abstract of a paper read before the 134th regular meeting

of the American Physical Society held at Portland, Oregon, 19 June 1925, the authors report that a group of strong bands, degraded to the red, extending from λ 1354 to λ 1854 A appeared in purified nitrogen at 0.003 mm pressure, using an arc discharge, a long tube, and flowing gas. Thirty bands were observed of which seventeen had been reported previously by Lyman.

Sponer, H., "The Excitation Potentials of the Band Spectra of Nitrogen", Z. Physik, 34, 622-633, (1925).

This paper contains an energy diagram for neutral molecular nitrogen (N_2) which was derived both from new data on the critical potentials required to excite the positive and negative bands and from data in the literature. The author also discusses the origin of active nitrogen in the afterglow. It is suggested that active nitrogen is atomic nitrogen and that the luminescence of the afterglow originates from the light emitted during the recombination of the nitrogen atoms.

It is pointed out that a trace of molecular oxygen is required to produce the afterglow and may act as a poison to the glass walls. The dissociation energy of N_2 is given within the following limits

$$11.4 < \text{Dissociation energy} < 13.0 \text{ volt.}$$

In calories this boundary limitation is between 260,000 and 296,000. The excitation potentials of the first and fourth positive bands are shown to be 9.3 and 14.8 volts respectively. The second positive bands appear at 13.0 volts. The excitation potential of the negative bands is shown in the diagram to be 19.6 ev. The ionization potential of molecular nitrogen is calculated to be 16.5 volts.

1926

Birge, R. T. and H. Sponer, "The Heat of Dissociation of Non-Polar Molecules", Phys. Rev., 28, 259, (1926).

This paper is a discussion of the heat of dissociation for the molecules O_2, N_2, CO, and NO. It is stated that the limiting amount of vibrational energy which a diatomic molecule can possess is given by the following expression.

$$E_n = h \int_o^{n_o} \omega^n \, dn$$

where ω^n is the frequency of vibration, as a function of the vibrational quantum number n, and n_o is the value for $\omega^n = O$.

In regard to nitrogen the authors state that the strongest bands observed in the afterglow of "active nitrogen" correspond to transitions from the level n = 11, of electronic level B of neutral nitrogen. By assuming that active nitrogen is atomic nitrogen, the authors conclude that the energy value of the level (the height above level X) is a measure of the heat of dissociation of N_2. The value obtained is 11.4 volts. A table of various heats of dissociation which the authors had obtained is given in the summary. Those for N_2 are:

Molecule	D from linear extrapolation (this paper)	D from band spectra	D from other sources
N_2	11.4 = 263,000 cal (from active nitrogen)	11.9 = 274,000 cal	11.4 = 263,000 cal [from active nitrogen Sponer (1925)]

Sponer, H., "Absorption Bands in Nitrogen", Nature, 118, 696, (1926).

Reference is made to the author's determination of critical potentials [Sponer, Z. Phys. 34, 622, (1925)] by measuring the excitation potentials of the O-O band of the second positive group and the negative bands. In the present experiments new absorption bands were observed in the extreme ultraviolet employing a vacuum grating spectrograph containing nitrogen at about 20 cm pressure. The bands had the same frequency differences as those of the final state of the first positive group, which constituted proof that the first positive group was emitted from the first excited state of the molecule. The O-O band of the new system corresponds to an excitation potential of 8 volts which confirmed the prediction of R. T. Birge and the authors.

1927

Birge, R. T. and J. J. Hopfield, "The Ultraviolet Band Spectra of Nitrogen", Phys. Rev., 29, 356, (1927).

This is an abstract of a paper read before the 142nd regular meeting of the American Physical Society 28-30 December 1926, Philadelphia, Pennsylvania. The authors report that the ultraviolet nitrogen system previously analyzed by them [Nature 116, 15, (1925)] had been greatly extented to include 60 bands between λ 1250 and λ 2025 A. Two other progressions of emission bands lying between λ 1030 and λ 1520 A were identified.

Constantinides, Philip A., "Electrical Properties and Nature of Active Nitrogen", Phys. Rev., 30, 95-108, (1927).

Reference is made in the introduction to the work of E. P. Lewis (1900) who described the nitrogen afterglow and to the systematic study of the physical and chemical properties of active nitrogen by R. J.

Strutt. The question of the degree of the purity of nitrogen necessary for the production of the afterglow is briefly discussed by citing the investigations by Compte, Tiede, Domcke, and Pirami who showed that it was impossible to produce the glow in very pure nitrogen.

Glowing active nitrogen from an electrodeless discharge tube was drawn in succession through two sets of coaxial cylindrical electrodes. The current between the electrodes of the second set was found to remain constant when the potential between the electrodes of the first set was varied from O to 250 volts. This was taken to indicate that the conductivity was not due to ions drawn from the discharge chamber. It was concluded that the current between electrodes in active nitrogen was due to electrons emitted from the surfaces of the electrodes either photoelectrically or by direct action of the active nitrogen on the metal.

Experiments on the ionization of foreign gases by active nitrogen indicated that it did not ionize hydrogen or mercury vapor. Experiments with iodine vapor indicated a considerable amount of ionization. From these observations the author concluded that the molecule of active nitrogen is molecular nitrogen in a metastable state with energy between 9.4 and 10.4 volts.

Crew, W. H. and E. O. Hulburt, "Pressures in Discharge Tubes",
Phys. Rev., 30, 124-137, (1927).

This report is concerned with the temperature and percentage dissociation of the following gases: He, H_2, O_2, N_2, air, CO, and CO_2 as functions of pressure and power input in discharge tubes. The increase in pressure of a gas in a discharge tube due to the discharge was measured for pressures from about 0.1 to 20 mm Hg. The pressure increase was regarded as due to the increase in temperature and to the dissociation of the gas molecules into atoms or less complex molecules.

Two discharge tubes were used in turn. The experimental details are fully described. Pressures below 1 mm Hg were measured by a striation gauge, which was a second discharge tube excited by direct current calibrated so that the shift of the striations of the positive column with pressure was known. Pressures from 2 to 20 mm were measured with an oil manometer.

The concentration γ of the atoms in the volume v' is defined by

$$\gamma = [\, n_2''/(n_2' + n_2'') \,]$$

and $$\gamma = 1 - \frac{T_2}{T_1} \frac{p_1}{p_2} \frac{v}{v'} + 1 - \frac{v}{v'}$$

In regard to nitrogen the present experiment indicated that atomic nitrogen was not produced in large quantity in the electric discharge at a fairly low pressure, and consequently that active nitrogen is perhaps the nitrogen molecule. The authors conclude that a few nitrogen atoms may very well exist and that these are responsible for the nature of the active nitrogen. As a reference for the latter statement the paper by Ruark, Foote, Rudnick, and Chenault (1927) is cited.

Hopfield, J. J., "Absorption Spectra in the Extreme Ultraviolet", Phys. Rev., 29, 356, (1927).

At the 142nd regular meeting of the American Physical Society held 28-30 December 1926 at the University of Pennsylvania, Hopfield reported his work on absorption spectra of nitrogen, air, acetylene, and carbon monoxide. With reference to nitrogen the spectra show strong continuous absorption beginning at λ 900 A. The principal lines of the four ultraviolet series of N I and a group of lines λ 1085 A due to ionized nitrogen were observed.

Kenty, Carl and Louis A. Turner, "Surface Layers on Tungsten Produced by Active Nitrogen", Nature, 120, 332, (1927).

The authors report their discovery that a fine tungsten filament undergoes a considerable (10.25%) lowering of its resistance when heated to a dull-red temperature and placed in a stream of active nitrogen. A detailed description is given of all the changes of the phenomenon observed. The authors conclude that a clean tungsten surface when heated to a dull-red and placed in an atmosphere of active nitrogen produced either by a condensed discharge or by electron bombardment at more than 22 volts, becomes covered with a nitrogen layer of the order of one atom deep. The effect of the layer is to cool the surface which apparently conducts more heat to the gas. The flashing of a filament covered with a nitrogen layer near a clean filament caused the production of a layer upon the latter. The layer evaporated by flashing was thought to come off in an active form. These experiments demonstrated that active nitrogen could be produced by bombardment of nitrogen gas with 22 volt electrons.

Ruark, Arthur Edward, Paul D. Foote, Philip Rudnick, and Roy I. Chenault, "Spectra Excited by Active Nitrogen", J. Opt. Soc. Am., 14. 17-27, (1927).

The authors state that the preponderance of evidence indicates that active nitrogen consists of neutral nitrogen atoms in an excited state, which explains qualitatively all the effects produced by active nitrogen. Reference is made to the theory that active nitrogen consists of metastable nitrogen atoms, and that Saha and Sur [Phil. Mag. 48, 421, (1924)] adopted this theory to explain the data. Reference is also made to some of the authors of the present paper who used this point of view [Phys. Rev. 25, 241, (1925) ; Nature 114, 750 (1924)].

The neutral nitrogen atom hypothesis was discussed by Miss Sponer [Z. Physik 34, (1925)]. The authors also state that indirect evidence for the atomic nitrogen hypothesis can be obtained from the defects of rival theories.

The experimental arrangements of the present investigation consisted of an electrodeless discharge bulb with accessory apparatus for photographing the spectra excited in the afterglow of active nitrogen. The following topics were investigated: a. the band spectrum of the afterglow, b. the afterglow spectrum of mercury, c. spectra of other elements in active nitrogen, and d. thermochemical evidence on the origin of spectra excited by active nitrogen.

The authors conclude that thermochemical data alone cannot give the mechanism of the origin of the spectra obtained in these experiments. A bibliography of 27 references is included which refer to previous study on the topic of active nitrogen.

Sponer, H. "Die Absorptionbanden des Stickstoffs." "The Absorption Bands of Nitrogen", Z. Physik, 41, 611-618. (1927).

The author states that nine absorption bands were observed in the vacuum ultraviolet between 1450 and 1226 A. The bands corresponded closely with the emission bands described by Birge and Hopfield. These were attributed to NO (nitric oxide) by Sponer. Since the bands appear in absorption they cannot be identical with the emission bands of nitric oxide. The author shows by a quantum analysis that the bands originate in the normal state of molecular nitrogen and correspond to the transitions O-m, where m = 1, 2, 3, ... 8.

Sponer, H., "Absorption Bands in Nitrogen", Proc. Nat'l. Acad. Sci., 13, 100-104, (1927).

The experiments described in the present paper were accomplished with a new continuous light source for the extreme ultraviolet which was described by Lyman [Astrophys. J. 60, 1, (1924) ; Nature 118, 156, (1926)]. Two band systems, one beginning at 1544 A and the other beginning at 1450 A were measured. The former system corresponded to the missing absorption bands in nitrogen. A table is included which gives the wavelengths, frequency differences, and quantum designations of the system beginning at 1450 A. The wavelength standards used for calculation in the table were Lyman-α 1215.68, nitrogen 1492.61, and nitrogen 1742.81 A. The wavelengths coincided very nearly with those which belong to corresponding bands in the ultraviolet emission system of nitrogen measured and analyzed by Birge and Hopfied (1925).

Willey, Eric John Baxter, "On Active Nitrogen, Part III. Active Nitrogen and the Metals", J. Chem. Soc., 2188-2196, (1927).

This paper is a study of the catalytic activity of certain metals in the form of fine filaments in accelerating destruction of the glow of active nitrogen. It was observed that the catalytic activity of the metals probably depended upon the stability of their nitrides. The metals studied were platinum, silver, zinc, iron, copper (smooth), copper (spongy), tungsten, and molybdenum. The energy of active nitrogen was found to be 46,600 calories per gram-mole. It was also shown that the process of destruction in the gas phase was bimolecular with respect to active nitrogen.

1928

Birge, R. T. and J. J. Hopfield, "The Ultraviolet Band Spectrum of Nitrogen", Astrophys. J., 68, 257, (1928).

This is an excellent paper on the ultraviolet band system of nitrogen. A plate showing the ultraviolet emission and absorption spectrum of N_2 in the spectral range 900 to 2100 A accompanies the article. In the historical introduction reference is made to Schumann's (1903) discovery of the ultraviolet band spectrum of nitrogen. Schumann found that 21 of the strongest bands were in the interval $\lambda\lambda$ 1383 to 1871 A. These were first measured by Lyman (1911). The apparatus used and the method employed in the present investigation are described.

In Table I the authors have listed the observed wavelengths of about 60 bands of the new ultraviolet system of nitrogen. The measurements of these wavelengths were based on the λ 1215.68 A line for hydrogen. Among other conclusions the authors state that there is strong evidence for the 9.5 volt value for the heat of dissociation of N_2 and that

they are inclined to accept this value.

Herzberg, Gerhard, "Uber das Nachleuchten von Stickstoff and Sauerstoff und den Einfluss der Wande hierauf", "The Afterglow of Nitrogen and Oxygen and the Influence of Walls Thereupon", Z. Physik., 46, 878-895, (1928).

In this investigation it was observed that the walls of the tube had a distinct catalytic effect. It is stated that the afterglow of nitrogen will not persist unless some other gas is present, and if the quartz tube is thoroughly baked out prior to the experiment.

Hinshelwood, C. N., "Active Nitrogen", Nature, 122, 404-407, (1928).

This is a survey of previous investigations upon the bright yellow glow that E. P. Lewis observed when nitrogen was excited by an electric discharge. Because the glowing gas had remarkable chemical properties it was named "active nitrogen" by Lord Rayleigh.

The author summarized three possible views of the nature of active nitrogen. a. Molecules of nitrogen excited in the discharge are metastable and have a long life time. b. Atomic nitrogen emerges from the discharge and then by recombination yields molecules at a high energy level which emit the spectrum. c. Nitrogen atoms emerge from the discharge and cause excitation of normal molecules in a three-body collision

$$N + N + N_2 \rightarrow N_2^* + N_2^* .$$

Kaplan, Joseph and Gunther Cario, "Active Nitrogen", Nature 121, 906-907, (1928).

In this letter to the editor of Nature, reference is made to the preliminary report which Kaplan presented before the American

Physical Society which stated that his recent experiments had demonstrated the presence of metastable molecules of nitrogen in active nitrogen.

The authors state that the long life of active nitrogen cannot be explained on the hypothesis that active nitrogen is composed of metastable molecules. Its long life and behavior in the presence of catalysts supports the theory that active nitrogen in atomic and metastable molecules is formed by the mechanism of recombination of nitrogen atoms into molecules.

Kenty, Carl and Louis A. Turner, "Surface Layers on Tungsten and the Activation of Nitrogen by Electron Impact", Phys. Rev., 32, 799-811, (1928).

A fine tungsten filament heated to 400°C and placed in active nitrogen is quickly covered with a nitrogen layer which produces a lowering of the resistance of the filament. A preliminary account of these experiments was reported in Nature 120, 332, (1927). A more detailed description of the conditions of the experiments is given in the present paper. Active nitrogen could be produced by bombarding molecular nitrogen with electrons of energy greater than 16.3 volts. The authors suggest that activated nitrogen formed by the impact of electrons is atomic nitrogen, although this has not been conclusively established.

Knauss, Harold P., "Band Spectra in the Extreme Ultraviolet Excited by Active Nitrogen", Phys. Rev., 32, 417, (1928).

This is a report of an investigation to study spectra excited in the afterglow beyond the limits of quartz and to determine whether the entire dissociation of nitrogen is available for the excitation. The apparatus and experimental procedure are briefly described. From the

experimental evidence obtained the author concludes that atoms and molecules in the afterglow are excited readily with energies probably not above 9.5 to 10 volts. He concludes also that the excitation is caused by a nitrogen molecule in one of a series of metestable states carrying the corresponding energy. The experiments appear to support the view that atoms of nitrogen combine to form an excited molecule responsible first for the emission of α bands and later for the excitation of other spectra.

Okubo, J. and H. Hamada, "Metallic Spectra Excited by Active Nitrogen", Phil. Mag., [7], 5, 372-380, (1928).

The introductory part of this paper contains fourteen literature references to previous work upon the subject of active nitrogen. This gives a brief but thorough review of the large number of investigations whose purpose it is to discover the real nature of the phenomenon.

Two theories are mentioned. The first is that of Saha and Sur [Phil. Mag, 48, 421, (1924)] who consider that active nitrogen is composed of nitrogen molecules in an excited state with an energy content of 8.9 volts. The second theory, published by Miss H. Sponer [Z. Physik 34, 622, (1925)], supposes that active nitrogen contains nitrogen atoms. When two nitrogen atoms collide with a neutral atom or molecule, the energy corresponding to the heat of dissociation of a nitrogen molecule can excite the neutral atom or molecule, yielding the spectra of the gas. H. Sponer gave a value of between 11.4 and 13.0 volts as the heat of dissociation of nitrogen.

The topics discussed in the present paper are: a. experimental arrangements; b. the spectra of the afterglow; c. the afterglow spectra of metals which include Hg, Cd, Zn, Mg, Na, K, Tl and Cd. d. interpretation and discussion of the results.

Ruark, Arthur Edward, "Notes on Active Nitrogen", Phil. Mag., [7], 6, 335-336, (1928).

The purpose of this note was to compare the results of the author's experiments with those reported by Okubo and Hamada [Phil., Mag., 5, 372, (1928)]. The topic considered was spectra excited by active nitrogen when it comes in to contact with metallic vapors. The causes of the discrepancy in the results are examined.

1929

Bay, Zoltan and Werner Steiner, "A Spectroscopic Method for the Detection of Unstable Intermediate Products in Active Gases and its Application to Active Oxygen, Nitrogen, and Hydrogen", Z. Physik Chem., B3, 149-161, (1929).

In the present paper as well as in two others [Z. fur Elektrochem. 35, 733-737, (1929) and Z. physik chem. B9, 93-127, (1930)] the authors have described their spectroscopic study of unstable intermediate products in active gases. The method and the apparatus are fully discussed. By means of a weak, constant vibratory discharge an emission spectrum was produced within the discharge generated in active nitrogen. This made it possible to identify intermediate products. It is reported that for the first time nitrogen atoms were detected in active nitrogen. The authors conclude that it is very reasonable that nitrogen atoms play an essential role in active nitrogen.

Cario, G. and J. Kaplan, "Das sichbare Nachleuchten des aktiven Stickstoffs", "Visible Afterglow of Active Nitrogen", Z. Physik, 58, 769-780, (1929).

This is a report of the investigation of the afterglow spectrum

of active nitrogen. The effect of temperature variations suggests that the bands of the first positive group observed in the afterglow are emitted by nitrogen molecules. The authors ascribe the bands of the first positive group in the visible afterglow to the emission from nitrogen molecules which are present in the active nitrogen in the metastable state (A_o = 8.2 v). These are excited to the B_6 and B_{12} levels. by collisions of the second kind with metastable nitrogen atoms in the ^2P (3.56 v) and ^2D(2.37 v) states. The recombination of nitrogen atoms to form molecules yields the energy to re-establish the metastable states.

Slipher, V. M.and L. A. Sommer, "The Nature of the Aurora Borealis Spectrum", Naturwiss., 17, 802, (1929).

The authors have reported that the λ 5577.350 A green line originates from transitions between metastable terms in the spectrum of neutral atomic oxygen and that the line is analogous to nebulium lines. Another line at λ 5206 A was found on spectrograms of the Lowell Observatory. This radiation was considered to be of similar origin within neutral atomic nitrogen spectrum $2P\ ^4S_{3/2} - 2P\ ^2D_{5/2,3/2}$. This has an excitation potential of 2.37 v.

Sommer, L. A., "Nocturnal Illumination of the Upper Atmosphere over Gottingen", Z. Physik., 57, 582-600, (1929).

A specially constructed spectrograph was used for observing the night sky luminescence in the upper atmosphere above Gottingen. The author reports that hitherto unknown bands, in addition to the known auroral line λ 5577.35 A and the two lines discovered by Lord Rayleigh and Slipher, were photographed and measured. The lines were of extremely weak intensity compared with the auroral line. Besides the well-known bands found in the laboratory and by auroral observations,

the second positive and first negative groups of the nitrogen molecule occur. An energy level diagram of the nitrogen molecule is given in Figure 2 of the paper. The author concludes with the statement that because of these observations the arguements of Lord Rayleigh, stating that the auroral and night-sky luminescences are two distinct physical phenomena, lose and important support.

Wrede, E., "Measurement of the Concentration of Monatomic Hydrogen, Oxygen, and Nitrogen", Z. Physik, 54, 53-73, (1929).

With reference to nitrogen it was possible to produce a few per-cent of atomic nitrogen by the usual method of excitation. Spark discharges yielded concentrations up to 30-40%. A recombination effect was observed.

1930

Bay, Z. and W. Steiner, "The Composition of Active Nitrogen: Demonstration of its Components and Conditions of Activation", Z. Physik Chem., B9, 93-127, (1930).

In this continuation of the authors' investigation of the nature of active nitrogen, the presence of metastable molecules in activated nitrogen is demonstrated. The apparatus employed is described in detail. The metastable nitrogen molecules could be swept out of the discharge with mercury vapors. The ordinary nitrogen afterglow was weakened by the presence of mercury vapor, while the Hg spectrum was excited up to the $4\,^3D$-triplets.

The addition of hydrogen increased the proportion of metastable molecules because nitrogen atoms are removed by hydrogen atoms. The hydrogen also was found to reduce the average electron velocity in the activating discharge. This spectroscopic investigation led the authors to conclude that active nitrogen is initially a mixture of atoms and

metastable molecules. The composition of active nitrogen was shown to be influenced by experimental conditions.

Hopfield, John J., "Absorption and Emission Spectra in the Region $\lambda\lambda$ 600-1100", Phys., Rev., 35, 1133, (1930).

This is a preliminary report of Hopfield's study of the ultraviolet light emitted by helium mixed with other gases. In the region $\lambda\lambda$600-1000 A helium gives a very strong continuous light. This continuous spectrum of helium was employed as a background for absorption studies. Strong absorption bands in this region λ 600-1100 A were obtained in nitrogen and oxygen.

Six bands, $\lambda\lambda$ 722, 694, 682, 675, 671, and 669 are distinct. They form an approximate Rydberg series and are probably due to electronic transitions from the normal level. The limit of convergence, 18.58 volts, corresponds to the ionization potential of the nitrogen molecule.

Hopfield, John J., "New Spectra in Nitrogen", Phys. Rev., 36, 789, (1930).

This is an abstract of a paper read at the 164-th meeting of the American Physical Society, 19-21 June, at the University of Oregon, Eugene, Oregon. Using helium as a continuous light source Hopfield found the absorption band spectra of nitrogen in the region $\lambda\lambda$ 600-1100 A. The bands observed below 750 A were at wavelengths 723.2, 694.2, 681.7, 675.2, and 671.2 A in absorption, and 715.2, 690.9, 680.1, and 674.3 A in emission. They form a molecular Rydberg series converging to a limit of 18.6 volts corresponding to one of the excited states of N_2^+.

Jackson, L. C., "The Stern-Gerlach Experiment with Active Nitrogen", Nature, 125, 131, (1930).

The author reports that a stream of nitrogen was activated with a condensed electrical discharge and then submitted to analysis by the Stern-Gerlach method. A screen coated with silver nitrate was observed to have a brownish-black trace when struck by a stream of active nitrogen. The trace obtained with active nitrogen gave mg = $\pm$ 1/3, a value characteristic of the $^2P_{1/2}$ state of the atom.

Reference is made to Kaplan and Cario [Z. Physik 58, 769, (1929)] who considered that the afterglow in nitrogen is caused by the interaction of a metastable nitrogen molecule in the $^3\Sigma$ state with metastable atoms in the ^2P and ^2D states. The chemical activity was assumed to be due to metastable atoms. The author considers the presence of the ^2P metastable atoms and their chemical activity to be established by his experiments.

Vegard, L., "The Spectra of Solidified Gases and Their Theoretical Atomic Meaning", Ann. Physik, [5], 6, 487-544, (1930).

This is an extensive and comprehensive discussion of the results of Vegard's investigations during a period of six years on the spectra of solidified gases in liquid hydrogen and helium. Cathode rays from 100 to 30,000 volts and canal rays were employed for excitation. A large portion of the paper is concerned with the spectra of nitrogen and and mixtures of nitrogen with argon.

Many tables of data are given of the analysis of the various band systems. Condon's theory is applied for a discussion of the intensity distributions. Solid N_2 energy states are compared with those of gaseous N_2. The study of auroral spectra led to the investigation of

spectra of the solid gases. A bibliography of 28 literature references to previous papers by Vegard is included.

1931

Kaplan, Joseph, "Metastable Molecules and Active Nitrogen", Phys. Rev., 37, 226, (1931).

This is an abstract of a paper read by Kaplan before the 167th regular meeting of the American Physical Society held at the University of California at Los Angeles, 12-13 December 1930. The author discusses his experiments in which strong uncondensed discharges were passed through mixtures of nitrogen and mercury vapor at pressures of about 5 cm. The spectra obtained showed the first positive group of nitrogen with an intensity distribution which resembled that observed in the nitrogen afterglow. The relationship to the auroral spectrum is mentioned.

Kaplan, Joseph, " A New Source of Active Nitrogen", Phys. Rev., 37, 1004, (1931).

The announcement is made that it is possible to produce the afterglow of active nitrogen in an uncondensed discharge. The discharge was produced by a 25,000-volt, 1-KW Thordarssen transformer at pressures from 0.1 to 5 mm Hg. Reference is made to the author's explanation that weak radiations of the auroral spectrum are due to the first positive bands of nitrogen arising in processes similar to those in active nitrogen. It is concluded that the atmosphere is really a huge discharge tube without walls, and that there is spectroscopic evidence for considering the auroral displays to be electric discharges at low pressures.

Kaplan, Joseph, "The Auroral Spectrum", Phys. Rev., 38, 582, (1931).

It is stated in this abstract of a paper read before the 171st regular meeting of the American Physical Society held at the California Institute of Technology, Pasadena, California, 15-20 June 1931, that the auroral spectrum had been almost completely reproduced in the laboratory. The comparison of the upper atmosphere to that of a discharge tube without walls suggested the experiments reported in the present paper. The air pressure within the discharge tube was 10^{-3} mm Hg. The band spectrum phenomena observed was explained on the hypothesis that the nitrogen molecule predissociates.

Slipher, V. M and L. A. Sommer, "On the Interpretation of the Aurora Spectrum", Publ. Am. Astron. Soc., 6, 230, (1931).

This is the abstract of a paper presented at the 42nd meeting of the American Astronomical Society held in Ottawa, 26-29 August 1929. The authors report their observations on the spectrum of the auroral display of 7 July 1928 viewed from Lowell Observatory. In addition to the usual auroral spectrum a very interesting line appeared near 5206 A which the authors attempt to interpret on the basis of the quantum theory.

The observed line

$$\lambda\ 5206\ \mathrm{A} = 2P\ {}^4S_{3/2} - 2P\ {}^2D_{5/2,\,3/2}$$

was interpreted as belonging to the spectrum of the neutral nitrogen atom. Reference is made to Kayser's Handbuch V, p. 57, which suggests that this line may be often present in the auroral spectrum. The energy of excitation of the line is 2.37 volts, $2P\,{}^4S_{3/2}$ being normal state of the nitrogen atom. The authors state that the lines λ 3470.2 and λ 10407.3 which should be much less intense have not yet been observed, and that the λ 5206 line by their interpretation indicated the presence of nitrogen atoms in the upper atmosphere during an auroral display.

Kaplan, Joseph, "The Auroral Spectrum", Phys. Rev., 42, 807, (1932).

In the present paper Kaplan reports that the first negative bands of nitrogen, which comprise most of the nitrogen radiation in the auroral spectrum, have been excited under conditions which suggest those in the aurora very closely. The experimental method is described and the observations are fully discussed. He states that the excitation of N_2^+ bands observed in the present experiment may be due to a large concentration of metastable nitrogen molecules in the $A\,^3\Sigma$ state. The experiments suggest the presence of metastable molecules of nitrogen in both the nitrogen afterglow and in the aurora.

Okubo, J. and H. Hamada, "On the Nature of Active Nitrogen", Phys. Rev., 42, 795, (1932).

The authors show in this discussion that the properties of active nitrogen are accounted for by considering active nitrogen to be essentially atomic nitrogen. The existence of metastable atoms assumed by Cario and Kaplan [Z. Phys., 58, 769, (1929)] is unnecessary. On the basis of the Franck-Condon principle two assumptions are made to support their conclusion. a. In the vibrational states with $v' = \sim 8$ in the metastable $A\,^3\Sigma$ state, and likewise for $v' = \sim 6$ in the upper $B\,^3\Pi$ state, the nuclear distances are nearly equal to those in the equilibrium position in the normal molecular state. b. The metastable $A\,^3\Sigma$ molecules (with the exception of the neutral unexcited molecules and atoms in active nitrogen) corresponding to the quantum numbers $v'' = 7$ or 8 are most numerous.

Vegard, Lars, "Results of Investigations of the Auroral Spectrum during the years 1921-1926", Geofys. Publ., Oslo, 9, No. 11, (1932).

The important conclusions which were drawn from the results of investigation on the auroral spectrum with reference to the composition of

the upper atmosphere are summarized.

a. The hydrogen-helium layer does not exist.

b. Nitrogen is the dominating component in the auroral region, apart from the strong green auroral line, and exists largely in the form of positive ions, N_2+.

c. The origin of the strong green auroral line λ 5577 A is uncertain.

Willey, Eric John Baxter and William Arthur Stringfellow, "On Active Nitrogen, Part IX. The Electrical Conductivity of Active Nitrogen", J. Chem. Soc., 142-152, (1932).

In this investigation it was found that active nitrogen was electrically conductive. The conductivity was thought to be due to ejection of electrons from the metal testing electrodes by deactivation of metastable molecules impacting upon them. Thus the conductivity was not considered to be the result of photoelectric emission. The heat of dissociation of the reaction

$$N_2 \rightarrow 2N$$

is given as 9.5 volts.

1933

Kaplan, Joseph, "The Auroral Spectrum", Phys. Rev., 43, 214, (1933).

This is an abstract of a paper read by Kaplan at the 181st regular meeting of the American Physical Society, 16-17 December 1932. Experiments are described in which the first negative bands of nitrogen, which comprise most of the radiation in the auroral spectrum, were excited under conditions simulating the aurora. Lines due to N^+ were absent. It is stated that the usual excitation of the N_2^+ bands in discharges at low

pressures produces these N^+ lines, but that they are almost entirely absent in the auroral spectrum. It is concluded that in the present experiments the excitation of N_2^+ bands are due to the large concentration of metastable nitrogen molecules in the $A\ ^3\Sigma$ state, and that this is evidence of their presence in both the aurora and the nitrogen afterglows.

Kaplan, Joseph, "Light of the Night Sky and Active Nitrogen", Nature, 132, 1002, (1933).

In this letter to the editor of Nature, Kaplan refers to the nitrogen afterglow described in one of his previous papers [Phys. Rev., 42, 807, (1932)] in which he showed that the visible spectrum of the discharge consisted of the first negative and the first positive bands of nitrogen, with a trace of the second positive bands. The afterglows of nitrogen previously reported consisted mainly of the first positive bands which originate on the $v' = 10, 11$, and 12 vibrational levels. The present afterglow is described as originating on higher vibrational levels such as 18, 19, 20, etc. There is also a strong excitation of the first negative bands emitted by N_2^+.

Reference is made to the work of Sommer [Z. Phys., 57, 582, (1929)] who pointed out that in addition to the green auroral line (5577 A), the light of the night sky contains the negative bands of nitrogen, thus making it similar to the aurora borealis in its spectrum. Kaplan states that his present experiment indicates that Sommer's conclusion was correct and furthermore that the excitation of the light of the night sky is like that of a nitrogen afterglow. An earlier experiment [Kaplan, Phys. Rev., 33, 154, (1929)] and the one reported here show that it is possible to reproduce completely the light of the night sky in the nitrogen afterglow.

Lozier, W. Wallace, "The Heats of Dissociation of Hydrogen and Nitrogen", Phys. Rev., 44, 575, (1933).

Reference is made to Condon (1930) who made predictions of the products of ionization of H_2 by electron impact. Bleakney (1930) was able to verify Condon's predictions using a mass-spectrograph. One of the predictions was that H^+ ions should be formed with kinetic energies of several volts. The author gives in the present article a detailed description of the construction of an apparatus for determining the heats of dissociation of CO and N_2. The procedure included measurement of the minimum kinetic energy of the bombarding electrons, which are able to produce atomic ions; the kinetic energy of the dissociating products was measured simultaneously.

By the Franck-Condon principle the kinetic energy lost by the impacting electron is converted into potential energy of the molecule, producing an unstable state of the molecule which immediately dissociates, part of the potential energy being converted into kinetic energy. The electron energy loss minus the kinetic energy of the dissociation products yields the potential energy increase of the dissociated molecule with respect to the normal molecule. This is equal to the heat of dissociation of the molecule plus the ionization potential of the atom and any excitation energy of the dissociation products.

The experimental procedure as well as discussions of the results on hydrogen and nitrogen are included. The author reports the following values as a result of his experiments.

$D(H_2)$	=	4.43	±0.03 v
$D(H_2+)$	=	2.59	±0.03 v
$D(N_2)$	=	7.90	±0.02 v
$D(N_2+)$	=	6.73	±0.02 v

Okubo, J. and H. Hamada, "On the Modification of the Intensity Distribution in the Band Spectrum of Nitrogen", Astrophysics J., 77, 130-140, (1933).

Some conclusions are made regarding the results obtained in the experiments reported in this paper on the band spectrum of nitrogen in the auroral spectrum. The experimental results seem to indicate that the negative and the second positive bands are similarly enhanced both in the aurora and in the experiments. The enhancement was shifted to bands of higher quantum numbers in auroral spectra. The authors explain this as probably due to the fact that electrons exciting the auroral spectrum have higher velocities than electrons in experimental discharge tubes. Potential energy curves for the $A\ {}^1\Sigma$ and $B\ {}^3\Pi$ states of N_2 are included in the discussion part of the paper.

Slipher, V. M., "Spectrographic Studies of the Planets", Mon. Not. Roy. Astron. Soc. (London), 93, 664, (1933).

Plate 16 in this paper is a spectrogram of the aurora on 29 May 1932. The λ 5206 A line of atomic nitrogen appears clearly in Figure 1 of Plate 16.

Slipher, V. M., "Spectra of the Night Sky, Zodiacal Light, The Aurora, and the Cosmic Radiations of the Sky", Trans. Ann. Geophys. Union, pp.125-127, (1933).

At the 14th annual meeting of the American Geophysical Union before the section on Terrestrial Magnetism and Electricity, Slipher reported his discovery, made at Lowell Observatory, that weak impressions of the typical auroral nitrogen bands could be photographed in the morning and evening skies. The conditions necessary were to

make brief exposures at the critical moment when the first, or last, traces of sunlight touch the high atmosphere. It was observed that these auroral bands were usually present and more intense in the sky toward the sun, and that these auroral nitrogen bands were never present during the dark of the night except when an aurora is present.

1934

Herzberg., and H. Sponer, "Heat of Dissociation of the Nitrogen Molecule", Z. Physik Chem., B 26, 1-7, (1934).

The authors report their discovery on intercombination bands in the spectrum of molecular nitrogen between the normal level $^1\Sigma_g^+$ and the first excited level $^3\Sigma_u^+$ and consider that this establishes the value of 6.14 ev for the first excited level. It is stated that the pre-dissociation limit of the upper state of the second positive bands of nitrogen would be 12.07 ev, which corresponds to dissociation into two nitrogen atoms each in the ^2D state of 2.37 ev. The heat of dissociation is then 7.34 ±0.02. An energy level diagram of molecular nitrogen and a discussion of active nitrogen are included.

Jones, H. A and A. C. Grubb, "New Features of the Nitrogen Afterglow", Nature, 134, 140, (1934).

The authors report the results of their study of the nitrogen afterglow formed by passing nitrogen containing 0.25 percent of oxygen through an uncondensed discharge produced by a 25,000-volt transformer. When the critical voltage was reached it was noted that a greenish yellow glow appeared with great intensity. The afterglow showed many of the colors of the aurora after certain adjustments of pressure, velocity, and voltage were made. When the discharge tube was immersed in a bath at 30°C the glow disappeared, but was intensified if the temperature

lowered to -20°C.

Two spectrograms of this afterglow are included in the paper. The spectrum shows in the visible region the first positive, the second positive, and the first negative N_2^+ bands of nitrogen, and the β bands of nitric oxide.

Kaplan, Joseph, "Active Nitrogen and the Auroral Spectrum", Phys. Rev., 45, 671, (1934).

In this paper Kaplan has described the experimental method by which the nitrogen afterglow was photographed in the visible and the near-ultraviolet. Four photographs of the spectrum obtained are included. The spectrum consists of the first negative bands of N_2^+, the first positive bands of N_2 (which originate on the vibrational levels $v' = 15, 16, 17, 18,$ and 19) and the second positive group of nitrogen.

It is concluded that the spectrum suggests a large concentration of metastable moelcules of nitrogen in the upper atmosphere during auroral displays.

Kaplan, Joseph, "New Band Systems in Nitrogen", Phys. Rev., 45, 675, (1934).

The new band system in nitrogen described in this paper has been produced for the first time under laboratory conditions in gaseous nitrogen. It had previously been observed by Vegard [Skriftet Utgitt av det Norske Videnskamps Akad., i Oslo I, Mat-Naturv. Klasse, No. 2, 1930,] in the luminescence of solid nitrogen and in the spectrum of the aurora borealis. Measurement of the lines shows that the lower state is the normal state of the nitrogen molecule. The upper state corresponds to a new level of the N_2 molecule, probably the $^3\Sigma$ level produced from two ^4S atoms. The bands are represented by the formula

$$v = [49,766 + (1460\ v' - 21\ v'^2) - (2345.16\ v'' - 14.445\ v''^2)]$$

Reference is made to Vegard [Geofys. Publ., 10, No. 4, p. 37, (1933)] who discussed the two bands 3202.7 and 3420 in the spectrum of the aurora. These bands are identified as members of this new band system obtained by Kaplan.

Kaplan, Joseph, "New Band System in Nitrogen", Phys. Rev., 45, 757, (1934).

In this abstract of a paper read before the 191st regular meeting of the American Physical Society held at Washington, D. C., 26-28 April 1934, Kaplan has reported the revision of measurements of the new band system of nitrogen first reported in Phys. Rev., 44, 947 (1934). The revision was made possible by employing a spectrograph of larger dispersion. It is stated that the upper state, or initial state in emission, corresponds to a new level of N_2, probably the $^3\Sigma$ level which is produced from two ^4S atoms. The bands of the system can be represented by the formula

$$v = [49,766 + (1460\ v' - 21\ v'^2) - (2345.16\ v'' - 14.445\ v''^2)]$$

Kaplan, Joseph, "New Band System in Nitrogen - an Addition and Correction", Phys. Rev., 45, 898, (1934).

G. Herzberg has given the following formula for the nitrogen bands reported by Kaplan (1934).

$$v = [49774.4 + (1446.46\ v' - 13.93\ v'^2) - (2345.16\ v'' - 14.445\ v''^2)]$$

As a result this gives a new interpretation for the initial electronic state which is taken to be the metastable A $^3\Sigma$ state. Assuming that the initial level is a new triplet level which dissociates into two ^4S atoms, the total vibrational energy should be either 1.2 or 1.7 ev depending on whether $D(N_2)$ is equal to 7.4 or 7.9 ev. Kaplan concludes that the initial level is the A $^3\Sigma$ state, and that the heat of dissociation of nitrogen is 7.4 volts.

Kaplan, Joseph, "Active Nitrogen and the Auroral Spectrum", Nature, 133, 331, (1934).

In this letter to the editor reference is made to Kaplan's letter in Nature, 132, 1002, (1933). At that time no photographs of the spectrum of the afterglow had been obtained. In the present letter a photograph of the spectrum of the nitrogen afterglow is shown. It is noted that with the exception of the green auroral line (5577 A) the afterglow spectrum is remarkably like the auroral spectrum. Both spectra are shown in Figure 1 of the letter.

Lozier, W. Wallace, "The Heat of Dissociation of N_2", Phys. Rev., 45, 840, (1934).

The author states that observation of the long sought inter-combination band system $A\ ^3\Sigma \rightarrow X\ ^1\Sigma$ in N_2 has made possible a new determination of the dissociation energy of N_2. Reference is made to Kaplan's paper [Phys. Rev., 45, 757, (1934)] in which he reported a value of 7.4 ev for $D(N_2)$. Lozier states that while this value might appear to be in disagreement with the 7.90 ev reported by his own (1933) electron impact measurements, it is, in fact, not the case. Possible interpretations are listed in the following table which is included in the paper.

$N^+ + N$	$D(N_2^+)$	$D(N_2)$	$D(N_2)$
$^3P + ^4S^0$	8.62 v	I. P. 5.86 v	9.79 v
$^1D + ^4S^0$	6.73	I. P. 7.75	7.90
$^3P + ^2D^0$	6.25	I. P. 8.23	7.42
$^3P + ^2P^0$	5.06	I. P. 9.42	6.23
$^1S + ^4S^0$	4.59	I. P. 9.89	5.76

The author states that if the value of 3.67 ev for D(A') (extrapolation of the vibration levels of the A' state of N_2^+) is lowered to 3.1 ev, D(N_2^+) becomes 6.25 ev and D(N_2) = 7.42 ev, which would be in agreement with the value 7.40 ev reported by Kaplan.

van der Ziel, A., "Predissociation in the First Positive Group of Nitrogen", Nature, 133, 416, (1934).

The electronic level diagram of the normal N_2 molecule is shown, giving both the electronic levels and the dissociation states. It is stated that predissociation in the $C^3\Pi$ level was first observed by G. Herzberg (1931) and later studied by D. Coster, F. Brons, and A. van der Ziel (1933). This predissociation was interpreted to be due to the $^2D + {}^2D$ dissociation state. Kaplan (1931, 1932) also used this interpretation of predissociation. It is concluded in the present paper that the perturbing level is not $^4S + {}^4S$ but that it may be $^4S + {}^2D$.

van der Ziel, A., "Predissociation in the First Positive Group of N_2 and its Bearing on the Electronic Level Diagram of the Nitrogen Molecule", Physica 1, 353-362, (1934).

The communication presented in this paper is an investigation of predissociation in the $B^3\Pi$ state of nitrogen. It was observed that the P, Q, and R branches have a sudden change in intensity at the same J-value. This predissociation was interpreted as being caused by a repulsive level formed by nitrogen atoms in a ^4S and a ^2D state.

An electronic level diagram of N_2 with the atomic states in which the different levels dissociate is shown in Figure 3 in the paper. The dissociation energies for the nitrogen terms are listed as follows from Table 3.

Molecular Term	Dissociates into	Dissociation energy in volts
X $^1\Sigma$	$^4S + {}^4S$	7.87
a $^1\Pi$	$^2D + {}^2P$	5.30
A $^3\Sigma$	$^4S + {}^2D$	3.56
B $^3\Pi$	$^2D + {}^2P$	5.95
C $^3\Pi$	$^2D + {}^2P$	2.30

A bibliography of twenty literature references is included.

Watson, William W. and Philip G. Koontz, "Nitrogen Molecular Spectra in the Vacuum Ultraviolet", Phys. Rev., 45, 561, (1934).

This is an abstract of a paper read at the 190th regular meeting of the American Physical Society held at New York, 23-24 February 1934. The authors report that with a high current discharge in flowing nitrogen gas as the source they have secured spectrograms in the λλ 2300 to 1000A spectral range. A 10-foot vacuum spectrograph, with 5.5 A/mm dispersion was employed in the investigation. Rotational lines of the (0, 1), (0, 4), (1, 5), (1, 6), (1, 7), and (2, 8) bands of the a → X system; (0, 14), (0, 15) and (0, 16) of the b' → X system; and (0, 12) of the c → X system were given quantum assignments. From their studies the authors give a value of 7.9 volts for $D(N_2)$, supporting the value obtained by Lozier [Phys. Rev., 44, 575 (1933)].

Watson, William W. and Philip G. Koontz, "Nitrogen Molecular Spectra in the Vacuum Ultraviolet", Phys. Rev., 46, 32, (1934).

The nitrogen molecular spectra have been photographed in the spectral region 900 to 2300 A. Reference is made to the studies by Birge and Hopfield (1928), and to Hopfield (1930) who found a large number of emission bands of N_2 in the 900 to 1300 A region. In the

present study the authors report the discovery of many new bands in the N_2 system with an origin at 1847 A, first discovered by Hopfield. Revised vibrational quantum assignments have been given. These show that the N_2^+ molecular ion is the emitter, having a lower electronic state identical with that of the first negative band system.

1935

Bűttenbender, G. and G. Herzberg, "Uber die Struktur der Zwiten positiven Stickstoffgruppe und die Pradissoziation des N_2 - Molekuls"
"The Structure of the Second Positive Nitrogen Group and the Predissociation of the N_2- Molecule", Ann. Physik, 21, 577-610, (1934-1935).

This is an extensive study of the nitrogen spectrum. Complete data and a detailed discussion are given. The authors have analyzed the fine structures of 8 bands of the second positive nitrogen group. The rotational constants for the electronic states C $^3\Pi_u$ and B $^3\Pi_g$ were determined. The energy of dissociation of the N_2 molecule was calculated to be 169.47 ± 0.11 kcal (7.35 ev).

Lord Rayleigh, "Active Nitrogen of Long Duration, Law of Decay, and of Increased Brightness on Compression", Proc. Roy. Soc., A151, 567-584, (1935).

This is an extensive report on the duration, decay, and increased brightness of active nitrogen. The influence of the vessel walls on the duration of the afterglow was studied. The effect of glass and coated glass surfaces was investigated. Other topics considered were the influence of gas pressure on the duration, the law of decay of the luminosity, and compression experiments.

It was found that the catalytic activity of the walls of the vessel could be reduced to a minimum by coating the blub with metaphosphoric acid.

Spealman, M. L. and W. H. Rodebush, "The Reactions of Some Oxides of Nitrogen with Atomic Oxygen and Nitrogen," J. Am. Chem. Soc., 57, 1474-1476, (1935).

Atomic nitrogen and oxygen were produced by passing the gases through an electrodeless discharge. The percentage dissociation was measured by a Wrede gage described by Rodebush and Klingelhoefer [J. Am. Chem. Soc., 55, 130, (1933)]. In regard to the reactions of the oxides of nitrogen with nitrogen atoms, the nitrogen was passed through the electrodeless discharge. In addition to atoms in the normal state, excited atoms and molecules in the $^3\Sigma$ A level may also occur. The latter should react with the oxides of nitrogen. In this investigation it was assumed that all species other than the normal atoms were present in negligible amounts.

When nitric oxide or nitrogen dioxide was added in small amounts to active nitrogen the characteristic afterglow (first positive bands) fades, and only a faint bluish glow is observed. Upon adding larger amounts the typical oxygen afterglow appears. A larger amount of nitrogen dioxide will quench the glow, but there is no change observed when nitric oxide is increased. The following reactions must occur:

$$N + NO = N_2 + O$$

$$N + NO_2 = 2\ NO$$

As soon as atomic oxygen is present the following reactions will occur

$$NO_2 + O = NO + O_2$$

$$O + NO = NO_2$$

The reaction

$$N + NO_2 = N_2 + O_2$$

was considered to be a much slower reaction.

The data are given in the following table, assuming reactions (a) and (b) are the only reactions taking place.

Total pressure	Pressure H_2O	Mole N_2	Mole NO_2 introduced	Mole NO formed	Percentage dissociation
0.44	0.002	0.013	0.00782	0.00086	1.7
0.50	0.13	0.010	0.00382	0.00112	2.8
0.37	0.0	0.015	0.0	0.00008	0.0

It is concluded that reactions (a) and (b) are fairly rapid. When the gases are pure and dry the dissociation is very slight. In the presence of water vapor or other impurity dissociation was readily obtained.

1936

Cario, G. and U. Stille, "The Origin of the Afterglow in Active Nitrogen", Z. Physik, 102, 317-330, (1936).

In the present paper the authors have discussed the existence of the negative bands and the higher members of the 1st positive group in the nitrogen afterglow. They state that certain of the band systems are pressure dependent. The wall effect is discussed and shown to be fundamental for the production of the afterglow.

Chapman, Sydney and W. C. Price, "The Upper Atmosphere - Nitrogen Absorption", Reports Prog. Phys. (London), 3, 56, (1936).

The authors state that molecular nitrogen is relatively transparent in the extreme ultraviolet, transmitting freely from the visible region of the

spectrum to 1450 A. Reference is made to the progression of narrow absorption bands of N_2 discovered by Birge and Hopfield (1928) in the 1450-1000 A region. The light must traverse a layer equivalent to 40 cm of nitrogen at N. T. P. in order for absorption to be complete in the center of these bands. This absorption is much weaker than that of O_2 in this spectral range. The sharp discrete nature of the nitrogen bands suggests excitation to stable excited states of molecular nitrogen rather than dissociation into nitrogen atoms.

Brief mention is made of the investigation by Hopfield (1930) who discovered that nitrogen bands in the 800 to 650 A region form a molecular Rydberg series converging to a limit at 661 A corresponding to an excited state of N_2^+. The authors conclude from available data on the extreme ultraviolet spectrum of N_2 that absorption on the short-wave side of 795 A (15.5 ev) and of 661 A (18.67 ev) will cause photo-ionization; in the 800-1000 A region the absorption causes excitation without ionization.

The excited states of N_2 leading to diffuse band spectra indicates a state of predissociation and would seem to be formed not directly by absorption of light from the ground state, but by absorption ($\lambda > 800$ A) from nitrogen molecules already excited by absorption from the ground state. These doubly excited nitrogen molecules may then dissociate into nitrogen atoms. This double process should occur only rarely because most of the first-excitation molecules will revert to the ground state before absorbing another quantum of light. As a result it is concluded that atomic nitrogen would be present in only very small amounts in the upper atmosphere. This is in accord with the fact that there is no evidence for the presence of atomic nitrogen in the atmosphere from either night sky or auroral spectra.

Déjardin, Georges, "The Light of the Night Sky", Rev. Mod. Phys., 8, 1-21, (1936).

The present paper by Déjardin is an extensive summary and evaluation of the light of the night sky. The author considers in detail the general characteristics of the spectrum of the night sky light from observations made prior to 1933. The recent researches, 1933-1935, are divided into three spectral regions for simplification: region 8000-5000 A; region 5000-3800 A; and ultraviolet region.

The author concludes from researches up to 1935 that the presence of lines of atomic nitrogen in the spectra of the night sky light is very doubtful. Sixty-three references to the literature are cited in the paper.

1937

Bernard, Rene, "Spectrum of Nitrogen and Atmospheric Pressure at High Altitudes", Nature 140, 930, (1937).

The author has observed in a series of experiments on the excitation of nitrogen bands by a controlled electronic bombardment that the spectrum can be modified greatly by varying experimental conditions. The intensity of the negative system of bands (emitted by N_2^+ ions) increases in comparison with that of the second positive system, when the pressure is decreased.

The author refers to Kaplan's (1937) proposal for obtaining the actual value of the atmospheric pressure between lower and upper boundaries (100 to 1000 km) of the auroral zone by seeking the pressure which permits the production of a laboratory spectrum similar to that of the aurora. Bernard points out that observation of auroral displays having a height of several hundreds of kilometers has shown that the spectral compositions are practically the same at each point. The influence of pressure should enhance the bands of the second positive system of nitrogen at the lower limit

of the aurora. Since this change has never been observed, it would be difficult to apply the influence of the afterglow spectrum to the upper atmosphere and be considered as a source of precise information.

Chapman, Sydney, "On the Productions of Auroral and Night Sky Light", Phil. Mag., 23, (7th series), 657, (1937).

The author in the first part of the present paper reviews the recent knowledge of the auroral and night sky light. Reference is made to Dejardin [Rev. Mod. Phys., 8, 1-21, (1936)]. The topics considered in Chapman's paper are: a. a theory of the night sky light and b. the auroral spectrum.

With reference to atomic nitrogen Chapman considers the impacts of external particles on nitrogen molecules, the latter dissociating into atomic nitrogen. From a study of the absorption spectra nitrogen is more readily ionized than dissociated. It was concluded that dissociation of molecular nitrogen was of minor importance in auroral spectra. The nitrogen atoms which are formed, if they are also excited, will radiate in the far ultraviolet. As a consequence atomic nitrogen should not contribute to the visible spectra of the aurora.

The contribution of nitrogen atoms to the night sky spectrum was considered less likely on account of the low energy of the main excitation process postulated by Chapman in this discussion. The author expresses doubt about Sommer's identification of the N I λ 5208 A on the plates of the night sky spectrum obtained by Slipher. Chapman prefers to agree with Dejardin (1936) that the presence of lines of atomic nitrogen in the spectrum of the night sky is doubtful.

Rabinowitch, E., "The Recombination-Velocity of Free Atoms", Trans. Faraday Soc., 33, 283-293, (1937).

The recombination-velocity of nitrogen is considered in the

present paper. Reference is made to the experiments of Lord Rayleigh [Proc. Roy. Soc., A151, 567, (1935)] which showed that the nitrogen afterglow could be observed with walls properly "poisoned" after the interruption of the discharge. The pressure of N_2 molecules was on the order of 10^{-2} mm and that of N atoms on the order of about 10^{-3} mm. The three-body reaction mechanism is expressed as follows:

$$N + N + N_2 \rightarrow N_2 + N_2 \text{ , which yields}$$

$$\left[\frac{d[N]}{dt} = C_1 [N]^2 [N_2] \right]$$

for the time of "half-decay", $t_{1/2} = \dfrac{1}{C_1 [N_2] [N_O]}$

where $[N_O]$ is the initial concentration of N-atoms

when $t_{1/2} = 3600$ sec., $[N_2] = 3 \times 10^{14}$ and $[N_O] = 3 \times 10^{13}$;

then $C_1 = 3 \times 10^{-32}$.

Saha, M. N., "On the Action of Ultraviolet Sunlight upon the Upper Atmosphere", Proc. Roy. Soc. (London), A 160, 155, (1937).

Since the ordinary solar spectrum extends to about λ 2913 A, the ultraviolet in shorter wavelengths is cut off by ozone absorption in the upper atmosphere. As a result there is no direct knowledge of the distribution of intensity in the solar spectrum beyond λ 2913 A. The author lists the following physical phenomena which are caused by the photochemical action of the extreme ultraviolet on the constituents of the upper atmosphere. These phenomena are: a. the luminous spectrum of the night sky, b. the ionization in the E and F ionospheric layers, c. the formation and equili-

brium of ozone, and d. magnetic storms and the electrical state of the atmosphere.

The following topics are discussed in this paper: a. the ultraviolet spectrum of the sun, b. the negative bands of nitrogen in the spectrum of the night sky, c. ionization of the nitrogen molecule in the upper atmosphere, d. distribution of elements in the upper atmosphere, and e. a general review of the spectra of nitrogen and oxygen.

Reference is made to Hopfield's experiments [Phys. Rev., 31, 1131, (1928), ibid., 36, 789, (1930)] in which it was concluded that light of wavelength λ 794 A could not directly ionize N_2 to N_2^+ normal state, that is, to a quantum having an energy content of 15.55 ev (X' level). The author suggests that is is quite probably that colliding electrons may have sufficient velocity that a number of N_2^+ (X') may be produced. The question as to whether nitrogen can be photochemically decomposed is discussed. It is suggested that one could expect the following process.

$$N_2\,({}^1\Sigma_g) + h\nu \rightarrow N\,{}^4S + N\,{}^2D \qquad E_1$$

$$N_2\,({}^1\Sigma_g) + h\nu \rightarrow N\,{}^4S + N\,{}^2P \qquad E_2$$

$$E_1 = D + N\,{}^2D - N\,{}^4S = 7.32 + 2.37\text{ V} = 9.69\text{ ev} = 1273\text{ A}$$

$$E_2 = D + N\,{}^2P - N\,{}^4S = 7.32 + 3.66\text{ V} = 10.98\text{ ev} = 1124\text{ A}$$

The wavelengths of the forbidden lines of atomic nitrogen are listed and the author states that as yet there is no definite evidence for the presence of forbidden lines of N I in the night sky spectrum but that this does not exclude the possibility of their occurrence.

Bernard, Rene, "The Forbidden Line of Atomic Nitrogen λ 3470 A in the Auroral and the Night-Sky Spectra", J. Phys. radium, 9, (Series 7), 157 S, (1938).

Reference is made to Kaplan [Nature, 141, 1139, (1939)] who recently had obtained the λ3471 A line in the afterglow under high pressure which corresponds approximately to the forbidden transition $^2P \rightarrow {}^4S$ of N I. Kaplan also pointed out that this line develops in the same way as the $A \rightarrow X$ bands of N_2 which were also present in his spectrograms.

Bernard states that he had observed these same effects in the spectra of certain diffuse auroras which would lead one to accept the presence of ^2P metastable nitrogen atoms in the upper atmosphere. Employing a comparison spectrum of neon, Bernard measured the wavelength of the auroral line to be 3466.5 ± 1 A. This new value is in excellent agreement with the theoretical wavelength (3466.6 A) computed from the ionization potential of the N I (14.58 V or 117,375 cm^{-1}) according to Hopfield.

The author states that the lines $\lambda\lambda$ 10,400 and 5200 A, which correspond to the $^2P \rightarrow {}^2D$ and $^2D \rightarrow {}^4S$ transitions of N I, might also be expected to occur in the auroral spectrum simultaneously with the λ 3466.5 A line.

Bernard, Rene, "Possible Presence of Metastable Atoms of Nitrogen (^2P) in the High Atmosphere", Nature, 141, 1140, (1938).

Bernard presents the results of an investigation in which he made a systematic study of the spectrum of different forms of auroras (arcs, draperies, clouds, coronas, etc.). An intense and sharp line near 3470 A

always appeared with the Vegard-Kaplan bands of nitrogen and could easily be distinguished from the neighboring bands.

As a plausible explanation it seemed reasonable to admit the presence of the atomic nitrogen line $^2P \rightarrow {}^4S$, the computed position being 3470 A. Reference is made to Kaplan's [Nature, 141, 645, (1938)] suggestion that the radiation at 3471 A in the night sky light reported by Dufay and Gauzit (1934) is perhaps the nitrogen line $^2P \rightarrow {}^4S$.

The author suggests that the presence of nitrogen atoms (^2P) in the auroral region should be taken into consideration and that the transitions $^2P \rightarrow {}^2D$ (λ 10,400 A) and $^2D \rightarrow {}^4S$ (λ 5206 A) might also be expected. Bernard concludes from the present state of knowledge that the mechanism of excitation in the aurora is: a. an electronic bombardment produces the permanent radiations in the spectrum; b. an afterglow gives rise to the nitrogen bands $A \rightarrow X$ and to λ 3470 A of N I ($^2P \rightarrow {}^4S$) radiation.

Bowen, I. S. and A. B. Wyse, "New Lines in the Spectra of the Gaseous Nebulae", Pub. Astron. Soc., Pacific, 50, 348-349, (1938).

The present note is a report of a search for the lines of additional chemical elements in the planetary nebulae. NGC 6572 and 7027 were observed with spectrographs attached to the 36-inch refractor of the Lick Observatory. Both objects were photographed on hypersensitized Afga Superpan Press film designed for the visible region. Among other new forbidden lines of O III, K VI, K V, Ca V, Fe VI, and Fe V the spectra showed the following transitions for atomic nitrogen:

Element	Transition	Wave Length Calculated	Wave Length Observed
N I	$^4S \rightarrow {}^2D_{3/2}$	5198.5)	5198.9
	$^4S \rightarrow {}^2D_{5/2}$	5200.7)	

Gauzit, J., "About the Ultraviolet Spectra in the Night Sky", Ann. astrophys., 1, 334, (1938).

This is a very comprehensive review of the ultraviolet spectra in the night sky. A list of 60 literature references is given. The question of the radiations of atomic nitrogen in the night sky is discussed and reference is made to the intense radiation λ 3471 A. The possibility of the existence of free atomic nitrogen, both normal and metastable states is examined. An energy level diagram of N I for the forbidden transitions, $^2P \rightarrow {}^4S$ (λ 3470 A), $^2P \rightarrow {}^2D$ (λ 10,407 A), and $^2D \rightarrow {}^4S$ (λ 5206 A) is included in the paper.

Gauzit, J., "Probable Dissociation of Nitrogen Molecules in the High Atmosphere", Nature, 142, 572, (1938).

The author refers to the discovery of line λ3471 A in the spectrum of the afterglow of nitrogen reported by Kaplan [Nature, 141, 645, 1139, (1938)] is probably corresponding to the forbidden transition $^2P \rightarrow {}^4S$ of N I. The line is emitted under relatively high pressure and at the same time as the Vegard-Kaplan bands which are also forbidden. Gauzit considers Kaplan's discovery applicable to the knowledge of physical conditions of the upper atmosphere.

Reference is made to Dufay and Gauzit [J. Phys., 5, (Series 7), 523, 527, (1934)] who observed the presence of an intense radiation at λ 3471 A in the spectrum of the night sky. Reference is also made to a paper by Bernard [Nature, 141, 1141, (1938)] who found that a radiation at λ 3471 A is also present in the spectrum of diffuse auroras where the Vegard-Kaplan bands are particularly intense. Gauzit in this letter to the editor makes two comments concerning the paper of Bernard's which confirmed the presence of metastable N I atoms in the upper atmosphere.

First Vegard and his collaborators probably observed the line λ 3471 A in the aurora but were unable to separate it from the second positive band near 3469 A. Second the line λ 5206 A corresponding to the $^2D \rightarrow {}^4S$ transition of N I has not yet been found in the night sky spectrum; however its presence in the spectrum of the aurora had been pointed out by Slipher and Sommer (1929). The latter workers mentioned that the line had been observed [Kayser, Handbuch der Spektroscopie 5, 57, (1910)]. Gauzit announces that he proposes to seek the presence of the λ 5206 A line of N I in the spectrum of the night sky and to study the radiation λ 3471 A in the night sky by the interferometer in order to ascertain the presence of nitrogen atoms in the high atmosphere.

Kaplan, Joseph, "The Preparation and Properties of Auroral Afterglows", Phys. Rev., 54, 176-178, (1938).

The preparation of auroral afterglows in pure nitrogen is described. A description is given for preparation of the discharge tube which consisted of a central Pyrex as quartz bulb (100 cc to 5 liters) with aluminum electrodes in side tubes.

When carbon and oxygen are present as impurities the following five distinct stages are observable: a. The ozone stage, b. nitric oxide stage, c. cyanogen stage, d. Lewis-Rayleigh afterglow, and e. the auroral stage. Each of these stages are briefly discussed. Two plates are included,one showing the spectrum of the discharge of pure nitrogen responsible for the production of the auroral glow and the second plate showing the spectra of the nitric oxide, cyanogen, and the auroral stages.

Kaplan, Joseph, "Where Does the Light of the Night Sky Originate", Phys. Rev., 54, 241, (1938).

In this abstract of a paper read at the 221st regular meeting of the American Physical Society held in San Diego, California, 22-24 June 1938, Kaplan reported that his experiments on producing afterglows in very weakly excited nitrogen, at low pressures suggest that the light of the night sky originates as low as the lowest auroral displays. Laboratory reproduction of a night sky spectrum shows such features as the Vegard-Kaplan bands, first positive bands originating on very high vibrational levels, second positive bands, cyanogen tail bands, and the new λ 3471 A line of nitrogen. The author states that these are all definite characteristics of the light of the night sky, and that most of the radiation originates in the lower regions of the upper atmosphere.

Kaplan, Joseph, "Wavelength of the New Nitrogen Line", Phys. Rev., 54, 541, (1938).

In this letter to the editor Kaplan reports a new measurement for the wavelength of the new nitrogen line $^4S \rightarrow {}^2P$ which he had previously reported as having a tentative wavelength of 3471 A. With an instrument of higher dispersion and employing a neon comparison spectrum there appeared to be no question as to the upper limit for the wavelength. The N I $^4S \rightarrow {}^2P$ line was found to lie a fraction of an angstrom unit on the short wavelength side of the strong neon line at 3466.578 A. A value of 3466.3 A represents an average from a series of measurements. Further work for better measurements was reported to be in progress

Kaplan, Joseph, "High Pressure Afterglow in Nitrogen", Nature 141, 645, (1938).

The presence of a strong line at a wavelength of approximately

3470 A in high-pressure (10 mm) afterglow in nitrogen is reported. The fact that this line is accompanied by the Vegard-Kaplan bands which are strong in the light of the night sky suggests that the line may be the hitherto unobserved atomic nitrogen ($^2P \rightarrow {}^4S$) whose predicted position is also 3470 A.

The author states that the auroral transition $^2P \rightarrow {}^2D$ should be much stronger than 3470 A in both the afterglow and in the light of the night sky. The radiation corresponding to the transition ($^2P \rightarrow {}^2D$) (infrared) has not been observed either in Kaplan's experiments or in the light of the night sky, and until it is observed the proposed identification of the 3470 A line as the trans-auroral transition $^2P \rightarrow {}^4S$ should be considered tentative.

Kaplan, Joseph, "A New Nitrogen Line", Nature, 141, 1139, (1938).

Reference is made to the author's preliminary study [Nature, 141, 645, (1938)] of a nitrogen afterglow at high pressures whose spectrum contained the line 3471 A which was tentatively identified as the hitherto unobserved transition $^2P \rightarrow {}^4S$ in atomic nitrogen. The author had made further study of the variations in intensity of the Vegard-Kaplan bands and the new line (3471 A). As the discharge tube approached the pure nitrogen stage the intensity of the λ3471 A line increased.

The author states that the absence of any of the forbidden transitions of non-ionized atomic nitrogen in the spectra of celestrial objects can probably be explained from the author's experiments in which he observed an enhancement of the Vegard-Kaplan bands and the 3471 A line with increase in pressure. This indicated that the forbidden transitions may occur at high pressures and that these radiations are possibly emitted at lower atmospheric levels, perhaps as low as 50 km.

Nicolet, Marcel, "Atomic Nitrogen in the Upper Atmosphere", Naturwiss., 26, 839, (1938).

The author reports that there is a line near 3471 A in the spectrum of the aurora borealis light and a line at 5206 A in the light of the night sky. Both of these are attributed to radiation of atomic nitrogen (N I). From calculations of the metastable excitation levels of N I, the value of 3466.5 A was obtained for the forbidden transition $^4S \rightarrow {}^2P$ and the wavelength values 5197.8 and 5200.1 A for $^4S \rightarrow {}^2D$. The author concludes that the difference between the calculated and observed values is too great and that some reservation should be employed in the interpretation of these auroral lines.

Vegard, Lars, "Atomic Lines in the Auroral Spectrum", Nature, 142, 670, (1938).

Reference is made to the letter published in Nature of 25 June 1938 by Bernard in which he had reported results of auroral spectrograms at the Tromso Observatory. In the present paper Vegard directs attention to the fact that all the experimental results had previously been described by Vegard and his collaborators.

The line λ 3470 A had been obtained and measured by Vegard in 1922 using a large quartz spectrograph [Phil. Mag., 46, 193, (1923) and Geofys. Publ., Oslo, 9, No. 11, (1932)]. The mean wavelength was 3469.4 A, and Vegard interpreted the line as the head of a band 2 P.G. (Second Positive Group) (3-4) (3469), while Bernard identified the line as due to a forbidden transition from the metastable (^2P) state to the normal (^4S) state of the neutral nitrogen atom as had Kaplan [Nature, 141, 1139 (1938)] on the basis of experiments in a nitrogen discharge tube.

In the present paper Vegard states that the great variation in intensity relative to other bands of the 2 P.G. could be accounted for if the atomic nitrogen line λ 3470 A also appeared with varying intensity. While the present observational data could not be considered as conclusive of the presence of the N I line, Bernard's interpretation was of particular interest in relation to other results obtained by Vegard and his co-workers. The following forbidden lines were considered as probably present in the spectrum of the auroral luminescence, indicating the presence of nitrogen and oxygen atoms in the auroral region.

	O II doublet	$({}^2D^0{}_2 \rightarrow {}^4S_{2,3})$	λ 3728.6 A
	O III lines	$({}^1S_0 \rightarrow {}^1D_2)$	λ 4362 A
and		$({}^1D_2 \rightarrow {}^3P_2)$	λ 5003 A
	N II lines	$({}^1S_0 \rightarrow {}^1D_2)$	λ 5751 A,
		$({}^1D_2 \rightarrow {}^3P_1)$	λ 6526 A,
	and	$({}^1D_2 \rightarrow {}^3P_2)$	λ 6543 A
	N I line	$({}^2P_{1,2} \rightarrow {}^4S^0{}_2)$	λ 3469.4 A

(as suggested by Bernard)

Vegard, Lars, "Occurrences and States in the Northern Lights Region", Geofys. Publ., Oslo, 12, No. 5, (1938).

In this paper Vegard reports that more than 80 oscillation bands of nitrogen can be identified in the spectrum of the northern lights. The intensity of the first positive group decreased rapidly with increasing altitude. It is stated that most of the weaker lines which have not been

definitely determined could be identified as O II and N II lines. The following wavelengths for N II lines are included in Table 2 in this paper: 5002, 4780, 4566, and 4226.3 A.

Worley, R. E. and F. A. Jenkins, "A New Rydberg Series in N_2", Phys. Rev., 54, 305, (1938).

The authors report some interesting features in the absorption spectrum of nitrogen below 1000 A. Two spectrograms are included which show the details of the spectral region 785 to 850 A at a pressure of 0.1-0.2 mm and path length 130 cm. The band systems terminate at about 800 A with a converging series of band heads. The limit of the series corresponds to 125,670 cm^{-1}, or 15.503 volts, which is the first ionization potential of N_2. This value was computed by Mulliken (1938) from data on the Hopfied absorption bands. The Lyman continuum was employed for light source.

Wulf, Oliver R. and Lola S. Deming, "On the Production of the Ionospheric Regions E and F and the Lower-Altitude Ionization causing Radio Fade-out", Terrest. Mag. Atm. Elect., 43, 283, (1938).

The purpose of this theoretical discussion is to account for the E and F regions by considering the absorption of ultraviolet radiation by nitrogen and oxygen molecules and their products. Reference is made to Koch [Arkiv. Mat. Astron. Fysik, 9, 1, (1913-1914)] whose study indicated two absorption regions in the extreme ultraviolet for nitrogen, the one at 810 A and the other at much shorter wavelengths. Chapman and Price regarded the absorption by nitrogen in the 800-650 A region much more intense than that in the 1000-800 A spectral range.

Wulf and Deming state that the absorption-peak in the shorter wavelength interval lies near 525 A. They suggest that this presumably represents the production of an excited molecule-ion or the production

of one normal and one ionized nitrogen atom; also the production of nitrogen atoms may occur in subsequent recombination-processes. It is suggested that the characteristic behavior of the F region may be due to the ionization of neutral nitrogen atoms and their high mobility.

1939

Bernard, Rene, "Presence of the Nitrogen Forbidden Line $^2P \rightarrow {}^4S$ in the Auroral Spectrum", Phys. Rev., 55, 511, (1939).

This is a brief note on the determination of the wavelength of the forbidden N I $^2P \rightarrow {}^4S$ line that had recently been observed by Bernard in the spectrum of diffuse auroras. The auroral radiation was found to practically coincide with the neon line λ 3466.575 A. Since the spectrograph employed was capable of distinguishing clearly lines only 3 A apart, Bernard affirmed that the true wavelength of the N I auroral radiation is 3466.5 ± 1 A.

Reference is made to the theoretical value λ 3466.6 A deduced by Hopfield from the ionization potential of N I (14.48 v or 117,375 cm^{-1}). Also Nicolet in a private communication to Bernard computed the value to be 3466.5 A from yet unpublished results of Edlen on the excitation potentials of the N I levels. From laboratory studies Kaplan (1938) reported a wavelength λ3466.3 A with an approximation of a few tenths of an angstrom.

Bernard concludes that the best measurements of the lines found near 3666 A in the afterglow and auroral spectra has indicated that the identity of these lines is highly probable, and has also established the presence of ^2P nitrogen neutral atoms in the upper atmosphere. Further, Bernard states that no night sky radiation could be identified with the N I line λ3466.5 A unless an error of 4 to 5 A was assumed in the measurement of the strong sky line found at λ3471 A.

Dufay, Jean, "About the Presence of Atomic Nitrogen in the Upper Atmosphere", Ann. astrophys., 2, 303, (1939).

This is one of the early papers by Dufay in which he has discussed the presence of forbidden lines of neutral atomic nitrogen in the auroral and night-sky spectra. A list of 27 references is included in the bibliography, citing the many observations that have been made on the nitrogen band emission in the night sky and aurora.

Kaplan, Joseph, "Atomic Lines in the Auroral Spectrum", Nature, 143, 278, (1939).

In this letter to the editor of Nature the author comments on a note by Vegard [Nature, 142, 670, (1938)] in which Vegard has interpreted the radiation at 3470 A in the auroral spectrum as the second positive group (3-4) nitrogen band. Kaplan makes reference to a report by R. Bernard on an auroral spectrum in which it was observed that the N_2 bands and the 3470 A line were unusually strong in comparison with the rest of the spectrum. Credit is given to Bernard for recognizing from this observation the strong resemblance between this auroral spectrum and the high-pressure afterglow spectrum discovered by Kaplan.

From the examination of a large number of afterglow and discharge spectra obtained in the laboratory and photographed by himself, Kaplan considers that the greater part of the radiation at 3470 A is due to the transition $^2P \rightarrow {}^4S$ in atomic nitrogen, and only a very small fraction to the 3 - 4 band of molecular nitrogen.

Kaplan, Joseph, "Excitation of the New Nitrogen Line ", Phys. Rev., 55, 598 (1939).

This is an abstract of a paper read at the 40th annual meeting of the American Physical Society held at Washington, D. C. 27-29 December 1938. The author refers to his discovery of the N I line at λ 3466.3 A

from high pressure nitrogen afterglows. Further studies on this line had been made and is reported in the paper.

Kaplan, Joseph, "A New Nitrogen Afterglow Spectrum", Phys. Rev., 55, 606, (1939).

This is an abstract of the second paper read by Kaplan at the meeting of the American Physical Society held in Washington, D. C., 27-29 December 1938. Two new characteristics of the spectrum of a nitrogen afterglow are reported. The first of these is the Goldstein-Kaplan band system of nitrogen. Their presence along with the first negative bands of N_2^+, the new N I λ3466.3 A line, the Vegard-Kaplan bands, and the second positive and first positive bands was suggested as possibly playing a significant role in the spectrum of the light of the night sky and in the auroral spectrum. The second new characteristic is the dimunition with pressure of the two transitions from metastable states (the 3466.3 A line and the Vegard-Kaplan bands). This also was suggested as of possible interest in upper atmospheric problems.

Kaplan, Joseph, "Forbidden Transitions in the Nitrogen", Nature, 143, 1066, (1939).

The forbidden transition $^2D \rightarrow {}^4S$ in atomic nitrogen at λ3466.4 A was observed in a high pressure afterglow in nitrogen. The weaker nebular line at approximately λ5200 A was also photographed on panchromatic plates. Experimental evidence indicated that high pressures and small volumes are favorable for the production of forbidden transitions.

Mitra, S. K. and A. K. Banerjee, "Atomic Nitrogen", Indian J. Phys., 13, 126, (1939).

In this excellent and extensive paper on the subject, "The Fringe of the Atmosphere and the Ultraviolet Light Theory of Aurora and Magnetic Disturbances", Mitra and Banerjee give a brief discussion about atomic nitrogen in the upper atmosphere. The following photodissociation processes are suggested for the production of nitrogen atoms.

$$N_2\,(^1\Sigma_g) + h\nu \xrightarrow{\lambda 1273\ A} N(^4S) + N(^2D)$$

$$N_2\,(^1\Sigma_g) + h\nu \xrightarrow{\lambda 1124\ A} N(^4S) + N(^2P)$$

The authors state that no such absorption corresponding to these processes has been observed in the laboratory. But spectroscopic evidence for the presence of atomic nitrogen in the metastable state has been obtained by the discovery of atomic lines corresponding to the transitions $^2D \rightarrow {}^4S$, and $^2P \rightarrow {}^4S$ in the night sky spectrum.

Nicolet, Marcel, "Mechanism of Excitation of the Forbidden Lines of Oxygen and Nitrogen in the Spectra of the Aurora and the Night Sky", Nature, 143, 639, (1939).

In this letter to the editor of Nature, Nicolet briefly reviews recent publications concerning the identification of the $^4S \rightarrow {}^2P$ forbidden transition of N I in the spectra of the aurora and night sky. Credit is given to Bernard (1938) who showed that the wavelength of the auroral radiation of this transition is 3466.5 A instead of 3470 A. Also laboratory investigations by Kaplan (1938) and theoretical determinations by Nicolet

(1938) give the values λ3466.3 A and 3466.5 A, respectively.

A new mechanism is suggested for the excitation of the forbidden line of N I. The mechanism does not require polyatomic compounds. Nicolet assum... at by collision of a normal O I atom with an N_2 molecule which has emitted the Vegard-Kaplan bands, the oxygen atom is actually only excited to the ^1D state and not to the ^1S state.

Since N_2 and O I are the major constituents in the upper atmosphere (above 100km) it seems likely that collisions must occur between these two constituents. Also if N I atoms are present in the high atmosphere the same mechanism explains the observation of the $^4S \rightarrow {}^2P$ forbidden transition associated with the emission of Vegard-Kaplan bands in the spectra of diffuse auroras. The excitation energy of the ^2P level of N I is 3.56 ev. It is assumed that a certain number of N_2 molecules after emission of the Vegard-Kaplan bands will collide with normal ^4S nitrogen atoms and bring them to the ^2P excitation state.

Nicolet, Marcel, "Forbidden Atomic Transitions in the Spectra of the Aurora and the Night Sky", Bull. classe Sci. Acak. Roy. Belg., 25, 81, (1939).

In this paper the author states that available data considering the relations between auroral or night sky radiations and the forbidden transitions of O II, O III, and N II do not confirm the existence of these ions in the upper atmosphere. The identification of the radiation λ3466.5 A in the auroral spectra with the $^4S \rightarrow {}^2P$ transition confirms the presence of N I in the auroral regions. There is also definite evidence of the radiations $\lambda\lambda$5577, 6300, and 6364 of O I in the upper atmosphere.

Richardson, R. S., "Intensity Changes in Bright Chromospheric Disturbances", Astrophys. J., 90, 368, (1939).

In section III of this paper the quantity of ultraviolet emission is discussed. The most probable source of ionizing radiation was considered to be the Lyman series, Lyman-alpha (λ1215.6)being the first member. From consideration of transition probabilities, a reasonable estimate for the minimum intensity of Lyman-alpha is about 5 times that of H_α in the Balmer series. Assuming the temperature of the sun to be 5740°K, the intensity of emission at H_α for a black body was computed to be 1.35×10^7 ergs, giving for Lyman-alpha a lower limit intensity of 6.75×10^7 ergs. Since the atmosphere is fairly transparent from $\lambda\lambda$1100-1300 A, light from Lyman-α can penetrate to a considerable depth. On the basis of several assumptions, the author determined the total radiation through this atmospheric "window" during a disturbance of more than average brightness to be about 60 per cent greater than normal.

1940

Bernard, Rene, "Conditions for Excitation of the Band Systems of the Neutral and Ionized Nitrogen Molecule", Ann. phys., 13, 5, (1940).

This is an extensive and thorough discussion of the conditions for excitation of the band systems of the nitrogen molecule. The electron-collision method was employed. Excitation was found to be most effective at 50 volts. The principal results are summarized as follows:

a. The energy of the exciting electrons can be computed from the relative intensities of the $N_2(^2P)$ and N_2^+ bands.

b. The application of the luminescence of nitrogen in the aurora borealis is considered.

c. The B $^3\Pi$ and C $^3\Pi$ bands of the neutral molecule of nitrogen have energies of 7.5 and 11 ev, respectively.

d. A study and interpretation of pertubations by dilution with monatomic gases were made.

e. The excitation of the Vegard-Kaplan bands of nitrogen with excess argon appears similar to the luminescence of the night sky.

Kaplan, Joseph, "Levels of Emission of Night-Sky Spectra",
Phys. Rev., 57, 249, (1940).

This is an abstract of a paper read at the 231st regulars meeting of the American Society held 22-23 December 1939 at the University of California, Berkeley, California. The amounts of atomic oxygen and nitrogen in the upper atmosphere, and the heights of origin of the green auroral line and the atomic nitrogen lines $^4S \rightarrow {}^2D$ in the night sky are considered. The discussion is based on the transition probabilities and on laboratory and field observations.

It is stated that if both radiations originate in the same regions of the atmosphere, there must be about 1000 times as much atomic nitrogen present as atomic oxygen, provided the excited states are produced at equal rates. The auroral green line may be emitted high in the atmosphere, while the nitrogen lines may be as low as the ozonosphere. The latter suggestion is in agreement with the observations of the enhancement of the nitrogen lines and the Vegard-Kaplan bands with pressure. Different mechanisms of excitation would then be responsible for the two radiations.

Kaplan, Joseph, " A New Afterglow Phenomenon", Phys. Rev., 57, 662, (1940).

The early and late phases of a nitrogen afterglow at a pressure of the order of 20 mm are reported. The forbidden nitrogen line 3466.5 A corresponding to the $^2P \rightarrow {}^4S$ transition is more intense in comparison with the second positive N_2 bands in the late phase than it is in the early part. It is reported that the spectrum of the late phase of an afterglow corresponds to that of the early phase of a higher pressure afterglow. The conclusion is that the effect on the spectrum of the afterglow as its life time increases is that of an apparent increase in pressure.

Kaplan, Joseph, "Temporal Effects in Nitrogen Afterglows", Phys. Rev., 58, 188, (1940).

This is an abstract of a paper read by Kaplan at the 235th regular meeting of the American Physical Society held at the University of Washington, Seattle, Washington, 18-21 June 1940. The author has reported continued experiments on the difference in spectra of nitrogen afterglows taken at varying times after the interruption of the discharge. It is reported that at 10 to 20 mm Hg the early phase of the afterglow showed intense first negative bands as well as strong $\lambda 3467$, making this the most faithful reproduction of the auroral spectrum. The actual intensity of $\lambda 3467$ was found to increase with time early in the afterglow even though the total intensity of the afterglow decreased. The author interpreted the results in terms of rapid predissociation of the nitrogen molecule and suggested that this rapid predissociation is the origin of forbidden lines in upper atmospheric spectra.

Pasternack, Simon, "Transition Probabilities of Forbidden Lines", Astrophys. J., 92, 129, (1940).

This paper is a re-examination of the calculations of transition probabilities of forbidden lines by Condon (1934) and others [Rubinowicz (1930) and Stevenson (1932)]. In Table 7c, p. 148 of the paper, transition probabilities for the $2p^3$ configuration are given for the N I lines $\lambda\lambda 3466.4$ (${}^4S_{3/2} \rightarrow {}^2P_{1/2}$), and 5200.7 (${}^4S_{3/2} \rightarrow {}^2D_{5/2}$), 5198.5 (${}^4S_{3/2} \rightarrow {}^2D_{3/2}$) A.

${}^4S_{3/2} \rightarrow {}^2D_{3/2}$	1.4×10^{-5} sec^{-1}
${}^4S_{3/2} \rightarrow {}^2D_{5/2}$	2.1×10^{-5} sec^{-1}
${}^4S_{3/2} \rightarrow {}^2P_{1/2}$	3.7×10^{-9} sec^{-1}
${}^4S_{3/2} \rightarrow {}^2P_{3/2}$	6.7×10^{-3} sec^{-1}

Schneider, Edwin G., "An Estimate of the Absorption of Air in the Extreme Ultraviolet", J. Opt. Soc. Am., 30, 128, (1940).

The author reports quantitative measurements on the absorption coefficients of air for about 350 points along the wavelength interval $\lambda\lambda 380$-1600 A. Table I in the paper gives the values of the absorption coefficient for these points. A brief description of the instrumentation and experimental procedure is included. Above the region 1300 A the air was introduced into an absorption cell with lithium-fluoride windows. For the spectral region below 1260 A a one-meter, 15,000 line to the inch glass grating was used at normal incidence. The light source was a "hot spark"

between a silver solder and a tungsten carbide electrode. Air at pressures between 0.1 mm and 0.005 mm was introduced into the body of the spectrograph.

Most of the absorption below 800 A was attributed to nitrogen. A few members of the series from 723 to 665 A, identified by Hopfield [Phys. Rev., 36, 789, (1930)], were resolved by the tungsten carbide line source to make their identification certain. Photographic measurements with oiled plates showed a strong absorption between 1300 and 1600 A and a quite transparent region between 1000 to 1300 A. It is concluded that this investigation presented a general picture of the amount and type of absorption to be expected within the spectral region $\lambda\lambda$380-1600 A.

1941

Bernard, Rene, "Atomic Nitrogen in the High Atmosphere", Ann. astrophys., 4, 13, (1941).

The forbidden radiation of atomic nitrogen N I $^4S \rightarrow {}^2P$ at λ3466.5 A was observed in the spectrum of the aurora. This radiation was absent in night sky luminescence. The line conforms in the aurora as the forbidden O I line and the A → X bands of molecular nitrogen. An energy level diagram for the forbidden lines of N I with wavelength values for the various radiations is included in the paper.

Dejardin, Georges, "Possible Presence in the Ultraviolet Radiation of the Nocturnal Sky of Bands of the Lyman Series due to Nitrogen Molecules", Compt. rend., 213, 360, (1941).

The author reports a large number of lines in the ultraviolet spectra of the night sky in the region $\lambda\lambda$2845-3313 A. The author states that below 3400 A the presence of both molecular nitrogen and ozone bands

may account for much of the observed spectrum.

Dejardin, Georges, "Spectrum of the Aurora of 1 March 1941 as observed by Dufay, Gauzit, and Tcheng Mao-Lin", Cahiers phys., 6, 42, (1941).

The results from laboratory experiments on the intensities of the radiation $\lambda\lambda$5206 and 4875 A under various conditions of excitation support the suggestion made by Dufay, Gauzit, and Tcheng Mao-Lin on the origin of these bands in the auroral spectrum.

Dufay, Jean, Junior Gauzit, and Tcheng Mao-Lin, "Spectrum of the Aurora of 1 March 1941", Cahiers phys., 1, 59, (1941).

The following features were reported as appearing in the spectrum of the aurora of 1 March 1941.

a. The auroral red lines of O I λ6300 A were more intense than the λ5577 A O I green line.

b. Bands of N_2 and N_2^+.

c. Bands at λ5206 A and λ4875 A of unknown origin.

The authors suggest that the radiation band 5206 A may be due to the $0 \rightarrow 3$ band of N_2^+.

Dufay, Jean and Tcheng Mao-Lin, "The Forbidden Doublet $^4S \rightarrow {}^2D$ of the Neutral Nitrogen Atom in the Auroral Spectrum of Low Latitudes", Compt. rend., 213, 692, (1941).

The authors report that during the auroral display on 18 September 1941 at the Observatory of Haute-Provence the radiation of wavelength λ5199 ± 1 A was observed using a spectrograph of medium dispersion. This was interpreted as establishing evidence of the forbidden doublet N I $\lambda\lambda$ 5197.8 – 5200.1 A, $^4S \rightarrow {}^2D$, in the auroral spectrum.

Gauzit, Junior, "The Presence of Forbidden Lines in the Spectra of the Night Sky and the Aurora, and the Constitution of the Upper Atmosphere", Compt. rend., 213, 695, (1941).

Reference is made to the investigations of Cabannes and Garrigue [Compt. rend., 203, 484, (1936)] who observed the radiation of the forbidden transition $^1D \rightarrow {}^3P$ 6300 A of O I. The green auroral line of atomic oxygen 5577 A (transition $^1S \rightarrow {}^1D$) is also discussed. The forbidden lines $^2P \rightarrow {}^4S$ at 3466 A and $^2D \rightarrow {}^4S$ at 5199 A of N I in the auroral spectra are considered. The author concludes that at altitudes of 100 km and above nitrogen and oxygen must exist almost entirely in the atomic state, and are the essential constituents in the upper atmosphere.

Götz, F. W. Paul, "A New Radiation in the Aurora Borealis of 18-19 September 1941", Naturwiss., 29, 690, (1941).

A spectrogram which shows the following lines and bands is included in the paper: λλ6300, 5577, 5190, 4708, 4278, 3914, and 3578 A. With the exception of the line at 5190 A these are the usual lines and bands of O I, N_2, and N_2^+. The line at λ5190 A was suggested as possibly the Ca line 5189 A.

Israel, H. and K. Wurm, "The Spectrum of Lightning", Naturwiss. 29, 778, (1941).

The authors report that the lines of O I, N I, O II, N II, H, and bands of N_2^+ were identified in the emission spectra of lightning. A table is included which gives wavelengths, the corresponding transitions, and excitation potentials of each of these radiations.

Vegard, Lars and E. Tönsberg, "New Important Results Relating to the Auroral Spectrum and the State of the Upper Atmosphere", Geofys. Publ., Oslo, 13, No. 5, (1941).

In the present paper the authors have discussed auroral and twilight spectrograms of which some were obtained at the Auroral Observatory at Tromso and others at the Physical Institute at Oslo. In all 27 spectrograms are included which, with the exception of one, were taken during the winter season of 1940-1941. Section 8 of the paper is devoted to the appearance of atomic nitrogen lines.

It is stated that some of the weak lines obtained in the auroral spectra during 1923 [Vegard, Phil. Mag., 46, 193, (1923); Z. Phys., 16, 367, (1923); Det. Norske Vid. Akad. Skr., I, No. 8, (1923)] might possibly be referred to the line spectra of nitrogen. Also after the atomic nitrogen spectra had been analyzed and the energy states had been determined for neutral and ionized nitrogen atoms, and when the strong green and red auroral lines had been established as belonging to the lowest energy states of the neutral oxygen atom, it was important to look for the corresponding lines of atomic nitrogen in the auroral spectrum.

In the following table (Table III in the paper) the wavelength values of N I are included which were taken from a paper by Nicolet [Inst. roy. Meteorol., Belgique XI, (1939)]. Nicolet had deduced the N I values from Edlens measurements of the energy states; the N II values were calculated from the energy states given by Bacher and Goudsmit [Atomic Energy States, London, (1932)].

N I		N II	
Transition	λ	Transition	λ
$^4S \rightarrow {}^2D_{5/2}$	5200.1	$^1D \rightarrow {}^3P_O$	6525.6
$^4S \rightarrow {}^2D_{3/2}$	5197.8	$^1D \rightarrow {}^3P_1$	6547
		$^1D \rightarrow {}^3P_2$	6583
$^4S \rightarrow {}^2P$	3466.5	$^1S \rightarrow {}^1D$	5754.8

Reference is made to Bernard who had pointed out that the N I line λ3466.5 A nearly coincided with a line in the auroral spectrum. It is stated that this line had been observed by Vegard in 1922, and since has been obtained on a number of spectrograms of considerable dispersion. The average wavelength values are included in Table 4 in the paper.

No.	Time for Exposure		Wavelength
1	Winter 1930-1931		3467.2
2	Winter 1934-1935		3467.9
3	Winter 1936-1937		3467.2
4	Winter 1940-1941		3467.7
		Mean	3467.5

The authors state that in 1938 Bernard obtained spectrograms at the Tromso Observatory which showed the same line as previously observed and measured by the authors of the present paper. Bernard first determined the wavelength of the line to be 3470 A which was very close to the accepted value of the N I ($^2P \rightarrow {}^4S$) line. Bernard proposed to identify the auroral line with this nitrogen line. Later Nicolet [Naturwiss., 26, 839, (1938)] gave the wavelength of the line to be 3466.5 A, and from repeated measurements on his spectrograms Bernard also determined the wavelength value as 3466.5 A.

From these results of Bernard and Nicolet there is apparently conclusive proof for the appearance of the N I ($^2P \rightarrow {}^4S$) line in the auroral spectrum. The authors in the present paper emphasize that Bernard's measurements cannot be regarded as definite with regard to the origin of the line situated near the N I ($^2P \rightarrow {}^4S$) line, but that it might be regarded as a possibility, and that the possibility has been supported by the authors' investigation.

1942

Debeau, David E., "The Nature of Reactions Occurring in the Production of the Afterglow of Active Nitrogen and the Effect of Temperature on the Phenomena", Phys., Rev., 61, 668-669, (1942).

An electrodeless discharge was applied to one of two connected glass bulbs filled with N_2 at a pressure of about 0.5 mm of Hg. During this process it was observed that the pressure of the system was nearly doubled while there was only a slight increase in the temperature. The intensity of the afterglow greatly increased when the second bulb was subjected to the temperature of liquid air.

Reference is made to the experiments of Lord Rayleigh [Proc. Roy. Soc., A176, 1, (1940)] who obtained about 10 ev per molecule from active N_2 in interaction with gold. This energy corresponds to that of completely dissociated N_2 with half the atoms in the metastable ^2D and the rest in the normal ^4S states. The following mechanism is suggested for the recombination:

$$N + N = (NN) \quad \text{(collision complex)} \tag{1}$$

$$(NN) = N + N \tag{2}$$

$$(NN) + M = N_2(B) + M \tag{3a}$$

$$N_2(B) = N_2(A) + h\nu \quad \text{(afterglow)}$$

$$(NN) + M = N_2(^1\Sigma) + M \tag{3b}$$

Since the energy radiated as afterglow is considered to be small compared with the energy present in the activated N_2, it was concluded that most of the impacts result in (3b) but that the few impacts resulting in (3a) cause the afterglow.

Dejardin, Georges and Jean Dufay, "The Ultraviolet Radiation of the Night Sky. I Description of the Emission Spectrum", Cahiers phys., 12, 35, (1942).

This report contains an extensive summary of all the emission lines and bands that have been observed and measured by various investigators of the emission spectrum of the night sky. The spectral region is from λλ4052 to 2844 A. A table is included which gives three groups of wavelengths: a. those regarded as certain, 36 being listed; b. 80 which are recorded as probable;and c. 40 which are considered possibly real. A bibliography is included which contains 25 references to previous work.

Dufay, Jean and Tcheng Mao-Lin, "Spectrum of the Aurora of 18 September 1941", Cahiers phys., 8, 51, (1942).

The authors report that the spectrograms obtained of the aurora on 18 September 1941 at the Observatory of Haute-Provence (Saint-Michel, Basses-Alpes) were characterized by forbidden red and green lines of O I as most prominent and the N_2 and N_2^+ bands next in prominence. Other emission features were observed and some of the lines were identified with unclassified N I lines.

Reference is made to the authors' previous paper [Cahiers phys., 1, 59, (1941)] on the spectrum of the aurora of 1 March 1941 in which the band at λ5206 A was suggested to be the $0 \rightarrow 3$ band of N_2^+. In the present paper it is reported that this line at 5206 A is assigned the wave-length 5198.9 A and identified as the forbidden transition $^2D \rightarrow {}^4S$ of N I. From intensity measurements the authors considered that due to the dissociation of molecular nitrogen many atoms are excited to the ^2D level but are unable to reach the ^2P level. According to the authors' hypothesis the transition $^2D \rightarrow {}^4S$ should appear more strongly than $^2P \rightarrow {}^4S$ N I line.

Elvey, C. T., "The Light of the Night Sky", Rev. Mod. Phys., 14, 140-150, (1942).

Reference is made in Section V of the present paper, Polar and Non-Polar Auroras, to the remarkable discovery by Slipher of the Lowell Observatory that during the "auroral flash" the negative bands of ionized nitrogen were present. In Figure 5 of the paper a series of

spectrograms of the "auroral flash" taken at the McDonald Observatory, Texas, are shown. The negative system of N_2^+, λ 3914 A, appears as a strong auroral band. The forbidden oxygen line 5577 A and the enhancement of red oxygen line λ 6300 A, as well as the λ 5893 sodium line, are also discerned. The author states that the presence of N_2^+ in the upper atmosphere is due to the ionizing action of the ultraviolet light of the sun.

Gauzit, Junior, "Constitution of the Upper Atmosphere: Dissociation of the Molecules of Oxygen and Nitrogen", Cahiers phys., 9, 47, (1942).

Brief mention is made in the paper of the recent identification of the forbidden N I lines, $^2P \rightarrow {}^4S$ at 3466 A by Bernard (1938) and $^2D \rightarrow {}^4S$ at 5199 A reported by Dufay and Tcheng Mao-Lin (1941). The greater portion of the paper is concerned with atomic oxygen in the upper atmosphere. An excellent bibliography of 25 references is included.

Gauzit suggests that atomic nitrogen is not only present during auroral activity but is always present in the upper atmosphere, and that above 100 km the nitrogen is present mostly as atomic nitrogen, the N_2 falling rapidly to a proportion of 10^{-4} at higher altitudes.

Götz, F. W. Paul, "Reply to the Remarks of L. Vegard", Naturwiss., 30, 752, (1942).

In this reply to Vegard the author states that the new line found by Götz was interpreted as the forbidden N I line λ5199 A. Götz also states that the forbidden N I line λ3467 A also appeared faintly in the spectrum.

Herman, Louis, "Presence of a System of Lyman Bands of the Nitrogen Molecule in the Ultraviolet Radiation of the Night Sky", Compt. rend., 215, 527, (1942).

This is a discussion of empirical formulas to represent the observed bands of the a $^1\Pi_u$ - X $^1\Sigma_g$ system. To account for the observed bands the Birge-Hopfield formula was extrapolated to v'' = 31.

Herman, R., L. Herman, and Junior Gauzit, "Spectra of the Night Sky in the Near Infrared", Cahiers phys., 12, 46, (1942).

This paper contains a brief account of the forbidden ^2P - ^2D radiation of atomic nitrogen in the spectrum of the night sky in the near infrared.

Herman, Renee, and Louis Herman, "Study of the Ultraviolet Spectrum of the Nitrogen Molecule", Compt. Rend., 215, 83, (1942).

The authors state that nitrogen emits several systems of bands in the ultraviolet. Reference is made to Kaplan (1934) who had reported a system of bands between $\lambda\lambda$2431-2741 A which were considered to have the same low energy levels as the system reported by van der Ziel [Physica 1, 353, (1934)]. If this analysis is correct the wave number differences of corresponding bands should be identical. To test this conclusion the authors photographed the Kaplan bands with a quartz spectrograph with a dispersion of 8 A/mm at 2500 A. It was found that the low levels of the two systems reported by Kaplan and ver der Ziel were not identical.

Nicolet, Marcel, "The Nitrogen Atom in the Upper Atmosphere", Bull. Soc. Roy. Sci., Liege, 11, 97, (1942).

This is a theoretical discussion of the excitation of the forbidden

N I lines in the aurora. It is concluded from intensity relationships that collisions of the second kind may not be neglected. There is a dependence of the intensity distribution of the N I and O I lines on the height points to a destruction of the equilibrium in the upper layers of the atmosphere.

Rayleigh, Lord, "Further Studies on Active Nitrogen. III. Experiments to Show that Traces of Oxygen or Other Impurities Affect Primarily the Walls of the Vessel, and not the Phenomena in The Gas Space", Proc. Roy. Soc., A 180, 123-139, (1942).

A brief summary is given of the main reasons for believing that nothing but pure nitrogen was involved in the phenomena of active nitrogen. a. Commercial nitrogen did not produce the afterglow well but became good after prolonged standing over moist phosphorus which removed the residual oxygen. b. the characteristic visual afterglow bands belong to the first positive group of nitrogen. c. the glowing gas reacted with cold merucury to form nitrides, and with hydrocarbons to form HCN. d. however, Comte (1913) and Tiede and Domcke (1913) found that the glow could be reduced to little or nothing when oxygen was completely removed, and could be restored when oxygen was intentionally admitted. e. the author found, though, that the restoration of the glow could be achieved by admitting a trace of gases other than oxygen, thus showing that the phenomena was not necessarily dependent on some reaction between nitrogen and oxygen.

The author concluded that the impurities had a catalytic action. The primary conclusion of the present paper was that the action of

oxygen must be on the walls of the tube. Various treatments of the walls of the vessel and the effect on the afterglow are also reported.

Rayleigh, Lord, "Further Studies on Active Nitrogen.IV. The Ionization Associated with Active Nitrogen", Proc. Roy. Soc. (London), A 180, 140, (1942).

The author announces that he has examined the ionization associated with afterglowing nitrogen more thoroughly than has yet been done. The experimental method is described in detail.

The ionization of nitrogen requires about 15.51 volts. The presence of this ionization would seem to cast some doubt on the attempts to calculate the energy of active nitrogen from the band spectrum emitted, which suggests an energy of 9.6 V. It is pointed out that previous investigations may have ignored the ionization phenomenon too much. The author shows that the ionization may, under certain conditions, involve as many atoms as the light emission.

Vegard, Lars, "Remarks on the Note of F. W. Paul Götz, A New Radiation in the Aurora Borealis of 18-19 September 1941", Naturwiss., 30, 752, (1942).

In this note Vegard comments that he (Vegard) had previously observed the line at λ5200 A reported by Götz [Naturwiss., 29, 690. (1941)], and that Vegard had found this radiation under high dispersion to be a complex, with a band and three lines.

Vegard, Lars, "Reply to the preceding Reply of F. W. Paul Götz", Naturwiss., 30, 752, (1942).

In this reply Vegard points out that the interpretation of Götz with reference to the forbidden N I line 5199A is not in accord with the intensities observed.

1943

Anand, B. M., P. N. Kalia, and Mela Ram, "Spectrum of Active Nitrogen in The Schumann Region", Ind. J. Phys., 17, 69-78, (1943).

This paper gives a review of the various theories of active nitrogen. The theories reviewed are: a. that of E. P. Lewis; b. the tri-nitrogen, N_3, of Lord Rayleigh; c. the hypothesis of Saha and Sur (1924); d. the hypothesis of Birge (1924); e. Sponer's theory (1925); f. the Cario and Kaplan theory (1929); g. the theory of Hebb and Sponer (1941). This review of the numerous theories suggests that atoms of nitrogen in some state are present in active nitrogen; however, the hypothesis up to the time of the present paper lacks direct experimental confirmation.

In the second portion the authors describe their own experiments to study the emission and absorption spectrum of the nitrogen afterglow in the Schumann region. The results of the experiments are discussed and compared with the existing theories. The present experiments appear to support the molecular nature of the phenomena rather than the atomic hypothesis.

Bamford, C. H., "Photochemical Processes in an Oxygen-Nitrogen Atmosphere", Reports Prog. Phys. (London), 9, 75, (1942-1943).

The following reactions involving atomic nitrogen are included in the paper.

Reaction	Remarks
(1) $N + N + M \rightarrow N_2 + M + 169$ kcal	possible recombination
(2) $N + O + M \rightarrow NO + M + 122$ kcal	possible recombination
(3) $N + NO_2 \rightarrow N_2 + O_2 + 116$ kcal	slow
(4) $N + NO_2 \rightarrow 2NO + 73$ kcal	fairly rapid
(5) $N + NO \rightarrow N_2 + O + 47.4$ kcal	fairly rapid
(6) $N + NO + M \rightarrow N_2O + M + 34.8$ kcal	does not occur readily
(7) $N + N_2O \rightarrow NO + N_2 + 134$ kcal	important
(8) $N + O_2 \rightarrow NO + O + 4.6$ kcal	no evidence for occurring
(9) $N + O_2 + M \rightarrow NO_2 + M + 53$ kcal	no evidence for occurring

Reactions (4), (5), and (7) were considered to be most important.

Dufay, Jean, "Forbidden Lines of Atomic Nitrogen in the Auroral and Night-Sky Spectra", Ann. astrophys., 6, 81, (1943).

The two radiations $\lambda\lambda$3466.5 ($^4S \rightarrow {}^2P$) and 5199 A ($^4S \rightarrow {}^2D$) are discussed in this paper. The line 3466.5 A ($^4S \rightarrow {}^2P$) was identified by Bernard, and the line 5199 A ($^4S \rightarrow {}^2D$) by Dufay and Tcheng Mao-lin in the spectra of the aurora. The author states that the λ3466.5 A line has never been identified clearly in the night-sky spectrum, nor has the presence of the λ5199 A line in the night-sky spectrum, nor has the presence of the λ5199 A line in the night-sky spectrum been established.

However the $^4S \rightarrow {}^2D$ line (λ5199 A) has been definitely identified in the auroral spectrum at low latitudes. During the aurora of 1 March 1941, at Saint-Genis-Laval, in cooperation with Gauzit and Tcheng Mao-Lin, Dufay photographed a very faint radiation next to 5200 A.

Again on 18 September 1941 at Saint-Michel (Basses-Alpes) the author obtained the same radiation with greater intensity. From their wavelength measurements Dufay and Tcheng Mao-Lin (1942) concluded that the wavelength was 5100 A for this radiation. During the same aurora Götz photographed the same radiation at Arosa and later obtained the value 5198 A for the wavelength, attributing it to the N I line.

Reference is made to Slipher and Sommer (1929) who identified the $^4S \rightarrow {}^2D$ line on 7 June 1928 in the auroral spectrum photographed at Flagstaff, Arizona. The author concludes that the presence of the λ 3466.5 A line in the "ordinary" aurora and of the λ5199 A line in the low latitude aurora emphasizes the importance of the dissociation of nitrogen molecules at high altitudes. Bernard (1941) estimated that nitrogen dissociation affects 1/15 of the N_2 molecules at the lower limits of the aurora and that it involves 3/4 at the upper limits. Dufay concludes that at the very high altitude of the aurora of 18 September 1941 the nitrogen must have been entirely dissociated by analogy with oxygen.

Gaydon, A. G., "The Band Spectrum of Nitrogen: New Singlet Systems", Proc. Roy. Soc. (London), A 182, 286, (1943).

The author states that the investigation of the nitrogen spectrum had for one of its objectives that of obtaining further information about the heat of dissociation of N_2. Although this object has not so far been achieved, the author reports that five new systems due to N_2 were discovered and analyzed. The amount of energy required to excite the fifth positive bands was considered to be no higher than 15.5 volts (125,000 cm^{-1}), which probably represents an upper limit rather than the actual excitation potential.

From the experiments described in the paper and a study of the conditions used by van der Ziel and by Kaplan it appears that the fifth positive bands have lower excitation levels than the new systems. The upper level of the fifth positive system probably lies below 105,000 cm^{-1}

Herman, Renee, "Auroral Spectrum of the Nitrogen Molecule", Compt. rend., 216, 492, (1943).

The author reports that in carefully controlled experiments, the green afterglow of nitrogen was observed to emit two different phosphorescent superimposed spectra. The new bands appear identical with the auroral band except in intensity.

Herman, Renee, "Identification of a New System of Bands of the Neutral Molecule of Nitrogen", Compt. rend., 216, 561, (1943).

The announcement that new bands of the neutral molecule of nitrogen observed in the ultraviolet spectrum is made in the present paper. Some of the bands are shaded toward the red, others toward the violet, and some are without band heads. The bands are associated with the 2nd positive group. Some of the bands correspond to those observed in the spectrum of the night sky.

Herman, Renee, "A New Forbidden Transition of the Neutral Molecule of N_2", Compt. rend., 217, 141, (1943).

In this paper the author reports a new series of bands of molecular nitrogen in the region λλ 2281.47 - 2795.6 A which are forbidden by symmetry selection rules. The lower level of the series is the same as the upper level of the Lyman bands, and the upper level coincides with the upper level of the band system reported by Koontz and Watson (1934). The bands corresponding to v' greater than 6 are weak or missing. The

author concludes that this is due to dissociation in the upper level of the Lyman bands into atomic nitrogen, ^4S and ^2D. Dissociation does not occur for pressures of 10 to 20 mm Hg, while bands in which v' is greater than 6 appear.

Herman, Renee, "Ultraviolet Spectrum of the Nitrogen Molecule", J. phys. radium, [8], 4, 245, (1943).

R. Herman reports in this paper more precise wavelength measurements of the band heads of a system first found by Kaplan (1934). A term diagram which correlates the various unidentified electronic states of the neutral nitrogen molecule is included in the paper. A wave number of 913 cm^{-1} is shown in the diagram. This is attributed to the series of molecular nitrogen even though this wave number is found also in the oxygen spectrum.

Herman, Renee and Louis Herman, "A New Band System of the Neutral Nitrogen Molecule", J. Phys. radium, [8], 4, No. 7, Suppl., 23, (1943).

The authors have made new measurements which led to the identification of a band system of molecular nitrogen in the spectral range λλ 2200 - 3300 A. The results are shown in Tables I and II in the paper. The following formula

$$\nu = \begin{Bmatrix} 42,460.7 \\ 44,169.6 \end{Bmatrix} + 1548.22\nu'' - 11.9\nu''^2$$

was derived for the band head of the new system.

Herman, Renee and Louis Herman, "Intensity Distribution in the Bands of Polar Auroras and the Temperature of the High Atmosphere", Cahiers phys., 15, 15, (1943).

The authors state that the values for the temperature of the high

atmosphere derived from relative intensities in the rotational structure of the N_2 bands observed in the spectra of polar auroras are in error. This is due to assuming that the nitrogen molecules are in thermal equilibrium in both the excited and ground states. While this assumption is true for ordinary pressures it does not apply to low pressures encountered in the upper atmosphere. The bands of the 2nd positive group of N_2 in which the number of molecules in the initial and final states depends only slightly upon temperature.

Worley, R. Edwin, "Absorption Spectrum of N_2 in the Extreme Ultraviolet", Phys. Rev., 64, 207, (1943).

This is an excellent study of the absorption spectrum of N_2 in the extreme ultraviolet. The excited states of N_2 in the range 12.2 - 17.0 ev were investigated. The spectral region was $\lambda\lambda$1015-730 A. The results are shown in Table I of the paper. From the new data obtained in this study it was possible to assign a slightly different value of the series limit v_∞ and to derive a Ritz formula to fill all but a few band heads.

The region of continuous absorption that follows the series limit was shown to correspond to unquantized photo-ejection of an electron from N_2, giving very precisely a value of 15.517 volts as the ionization potential of N_2. Numerous bands which do not form obvious series of the Rydberg type are referred to in the paper as "non-Rydberg bands". These discrete bands were found in the $\lambda\lambda$ 995-818 A spectral region. The investigation also included the determination of the rotational constant B' and a study of the v' progressions.

Wu, Ta-You, "Excitation Processes in the Night Sky and the Aurora', Indian Acad. Sci. Proc., 18 A, 40, (1943).

In this extensive paper on excitation processes in the night sky and the aurora the author considers the following two sources of information: first, the behavior of the ionized layers towards radio waves and the magnetic variations; second, the analysis of the spectra of the night sky and the aurora. The following main features of the spectra and the aurora are extensively treated in the paper.

a. The forbidden lines of O I
b. First negative bands of N_2
c. Vegard-Kaplan bands of N_2
d. First positive bands of N_2
e. Second positive bands of N_2
f. Lyman-Birge-Hopfield bands of N_2
g. Atmospheric bands of O_2
h. Schumann-Runge bands of O_2
i. The yellow lines of Na
j. Water vapor bands

The author assumes that the atmosphere is composed mainly of N_2, a smaller amount of O_2, the rare gases, and water vapor, a result of dissociation and ionization of the N_2 and O_2 molecules by ultraviolet solar radiations, N and O atoms, N_2^+, O_2^+, N^+, and O^+ ions are also present. The primary processes for production of atomic nitrogen are:

$$N_2\ (X\ ^1\Sigma) + h\nu\quad (\lambda < 1000\ A) \longrightarrow 2N\ (^2P)$$

$$N_2\ (X\ ^1\Sigma) + h\nu\quad (\lambda < 1200\ A) \longrightarrow N\ (^2D) + N\ (^2P)$$

The positive ions of N_2 molecules and N atoms may be produced as a result of photoionization by the solar radiations of very short wavelength. There is also the possibility that the metastable $N_2\ (A\ ^3\Sigma)$ formed from atomic nitrogen processes (described in the paper) may contribute greatly to the ionization by absorption of ultraviolet radiations of longer wavelength:

$$N_2\ (A\ ^3\Sigma) + h\nu \rightarrow 2N$$

$$N\ (^4S) + N\ (^4S) + X \rightarrow X + N_2\ (A\ ^3\Sigma) \quad v' \text{ up to } 7$$

$$N\ (^4S) + N\ (^4S) \rightarrow N_2\ (A\ ^3\Sigma) + h\nu$$

Assuming that atoms and molecules of nitrogen and oxygen are present in the upper atmosphere but that no radiations remove the metastable $N_2\ (A\ ^3\Sigma)$, for example after sunset, the author lists twenty three excitation processes in the upper atmosphere in Table II of his paper. The forbidden lines of N I $^2D \rightarrow {}^4S$ are discussed.

The author summarizes his paper with the conclusion that the main features in the selective emission spectra of the night sky and aurora are the forbidden O I lines and the various systems of bands of N_2^+, N_2, and O_2. The enhancement of certain lines and bands relative to others and the diurnal variations of certain lines in the night sky are considered to be satisfactorily explained by the theory that all the excitation and quenching processes in the upper atmosphere are collisions of the resonance type between the metastable atoms and molecules of nitrogen and oxygen. The metastable atoms are produced during the night by collisions between the metastable molecules, the latter being formed by recombinations of normal atoms which are produced by photodissociation of the molecules during the day. The author considers

the absence of certain atomic nitrogen lines in the night sky and the aurora a strong arguement for his theory, since the maximum energy available for the excitations in these metastables is only 6.1 volts, which is the energy of N_2 (A $^3\Sigma$).

1944

Gauzit, J., "The Composition of the Upper Atmosphere According to the Dissociation of Oxygen and Nitrogen Molecules", Bull. Am. Meteorol. Soc., 25, 245, (1944).

The author presents a theory that oxygen and nitrogen are entirely dissociated into the atomic state above 100 km, and that the molecules are present only as traces. Reference is made to the identification of forbidden lines λ 3466 A by Bernard [Nature 141, 1140, (1938); Bull. Soc. Franc. Phys., 10, 157, (1939)] and λ 5199 A by Dufay and Tcheng Mao-Lin [Compt. rend., 213, 692, (1941)] in the auroral spectra. However the author states that the identification of these two lines in the night sky spectrum is doubtful.

It is postulated that since the dissociation by absorption of ultraviolet light does not happen in the polar regions during the long night periods, intense air circulation at high altitudes transports the air masses of the upper atmosphere to establish the same composition over the entire higher altitudes.

Gaydon, A. G., "The Band Spectrum of Nitrogen: New Singlet Systems", Proc. Roy. Soc., A 182, 286-301, (1944).

In the present paper Gaydon has given in detail analyses of the nature and energy of five new electronic states of N_2. The following systems are reported:

a. System P, p $^1\Sigma_g^-$ to a $^1\Pi_u$

b. System Q, q $^1\Pi_g$ to a $^1\Pi_u$

c. System R, r $^1\Sigma_g^-$ to a $^1\Pi_u$

d. System S, s $^1\Sigma_g^-$ to a $^1\Pi_u$

e. System T, t $^1\Sigma_g^-$ to a $^1\Pi_u$

The discussion includes a review of the fifth positive or van der Ziel's system and Kaplan's first and second systems. Seven spectrograms are shown and briefly described.

Gaydon, A. G., "Dissociation Energy of Nitrogen", Nature, 153, 497, (1944).

Reference is made to van der Ziel [Physica, 4, 373, (1937)] who had observed weak predissociation in the first positive system of N_2 for bands with v' greater than 11. Van der Ziel concluded that the Δ type state cuased the predissociation. As a result the dissociation limit was considered to lie below the energy of the predissociation. The predissociation limit for the c $^3\Pi_u$ state was known to be 12.145 ev. This gave a value of 7.383 ev for the dissociation energy of N_2.

Gaydon and Penny [Nature,. 150, 406, (1942)] had shown that if the 7.383 ev value was correct, the rule that potential energy curves of molecular states of the same species may not cross would be violated. Gaydon in the present paper shows that van der Ziel's explanation of the predissociation is not the only one possible. The author considers that predissociation might equally well result from a repulsive $^5\Sigma_g$ state arising from $N(^4S)$ + $N(^4S)$, the lowest dissociation products for N_2.

It is concluded that this latter explanation is preferable since for the potential energy curves is maintained. The value 9.764 ev is given by Gaydon for the dissociation energy, $D(N_2)$ of nitrogen, and this leads to D(NO) = 6.49 ev instead of 5.29 ev for the dissociation energy of nitric oxide.

Wu, Ta-Your, "On the Existence of Atomic Nitrogen in the Upper Atmosphere of the Earth", Phys. Rev., 66, 65, (1944).

In the introduction to this paper the author states that partly on the basis of the observed spectra of the night sky and aurora and partly on the basis of the absence in the laboratory of continuous absorption by the N_2 molecule leading to dissociation

$$N_2 + h\nu \longrightarrow N + N,$$

many investigators consider that in the upper atmosphere oxygen exists in the atomic state and nitrogen in the molecular state. Several arguments are presented in the paper that atomic nitrogen may exist in the upper atmosphere.

One of the reasons for believing that nitrogen exists in the molecular state in the upper atmosphere is that the forbidden lines $^4S \longrightarrow {}^2P$ and $^4S \longrightarrow {}^2D$ of N I are absent in radiations in the night airglow and the aurora. Reference is made to Kaplan [Phys. Rev., 56, 858, (1939); ibid., 57, 249, (1940)] who suggested the possible presence of the $^4S \longrightarrow {}^2P$ line in the spectrum of the night sky. The author states that the transition probability of $^4S \longrightarrow {}^2P$ is of the order of 1 per second that the lifetime of the ^2P state is comparatively short, and that any N (^2P) atoms produced by dissociation by solar radiation will rapidly settle down into the states ^2D and ^4S on the emission of the lines $^2D \longrightarrow {}^2P$ and $^4S \longrightarrow {}^2P$. The lifetime of the ^2D state is of the order 10^{-5} seconds so that the failure to observe the $^4S \longrightarrow {}^2D$ line may be due to an insuf-

ficiently large number of N (^{2}D) atoms. As a result there may be considerable N (^{4}S) and N (^{2}D) atoms without revealing themselves in the spectrum if N (^{2}P) atoms are not excited by proper and frequent processes in the night sky and the aurora.

A second main reason for believing in the absence of atomic nitrogen in the upper atmosphere is the absence of continuous absorption by N_2 down to 600 A in the ultraviolet that leads to the dissociation of the nitrogen molecule. Several mechanisms of dissociation are given in the paper which may result from the many theoretically possible molecular states of nitrogen. It is pointed out that these mechanisms are theoretically possible provided that there are radiations of sufficiently high frequency. Astrophysical evidence appears to strongly favor these frequencies.

The following consequences are given if atomic nitrogen should exist in the upper atmosphere. The dissociation of N_2, on account of the smaller mass of the N atom, will lead to a greater density at a given height than that of an N_2 – O atmosphere. Thus assuming that N_2 and O are in diffusive equilibrium above ~ 150 km, the air density in the F layer (~250 km) is about 1/5000 of that in the E layer. But from observed collision frequencies by radio wave experiments the air density in the F layer is known to be about 1/30 of that in the E layer.

The author also states that the dissociation of N_2 will also give rise to an ionized layer due to the ionization of the N atoms. The variation of the degree of dissociation with height is not yet known; if it were, it would be possible to calculate the height of this ionized layer and hence contribute to a better understanding of the ionized layers.

Bernard, Rene, "Concerning the Wavelength of the Line N I ($^4S \rightarrow {^2P}$) of Atomic Nitrogen in the Aurora Borealis", J. phys. radium, [8], 6, No. 12, 29 S, (1945).

Reference is made to Bernard's [Nature, 141, 1140, (1938)] suggestion of the possible presence of metastable atoms of nitrogen (^2P) in the high atmosphere. The author also makes reference to the report of Kaplan [Nature, 141, 1139, (1938)] of a new nitrogen line λ 3471 A observed in the study of the nitrogen afterglow. In the present note Bernard reports the measurement of the wavelength of atomic nitrogen in the spectrum of the aurora borealis. The value $\lambda 3466.5 \pm 0.5$A was obtained. The author states that definite evidence is thus established for the presence of the line N I ($^4S \rightarrow {^2P}$) in the spectrum of the aurora.

Gaydon, A. G. and W. G. Penny, "The Dissociation Energies of CO, N_2, NO, and CN", Proc. Roy. Soc., A 183, 374, (1945).

The authors state that no previous set of values of the dissociation energies of CO, N_2, NO, and CN can be regarded as satisfactory unless violations of the non-crossing rule are postulated as possible. The non-crossing rule of Hund, and Neumann and Wigner (1929) is discussed. With respect to the dissociation energy of N_2 reference is made to van der Ziel (1934, 1937), who found a weak predissociation in some of the upper vibrational levels of the B $^3\Pi_g$ state. This predissociation occurs at 9.844 ev. Van der Ziel interpreted the predissociation as due to a repulsive Δ state and this lead to an assignment of $D(N_2) = 7.383$ ev.

In order to interpret van der Ziel's predissociation the authors of the present paper considered that near the crossing of the potential curves of B $^3\Sigma_g$ and $^5\Sigma_g^+$ it is possible for a range of J values in the stable Π state to change spontaneously to the same J value in the Σ state. With

this interpretation of van der Ziel's predissociation of N_2, Gaydon and Penny obtained the value $D(N_2) = 9.764$ ev. No violation of the non-crossing rule is indicated by this value. Accordingly the following values are given.

$$D(CO) = 11.11 \text{ ev} = 256.1 \text{ kcal.}$$

$$D(N_2) = 9.764 \text{ ev} = 225.1 \text{ kcal.}$$

$$D(NO) = 6.49 \text{ ev} = 149.5 \text{ kcal.}$$

$$D(CN) = 7.5 \text{ ev} = 174 \text{ kcal.}$$

Herman, Renee, "The Molecular Spectra of Nitrogen", Ann. Phys., 20, 241, (1945).

This is an extensive study of the molecular spectra of nitrogen. The author describes new results obtained which include measurements of the Lyman system. New bands in the system of Van der Ziel and the new systems γ, ∂, ϵ, ζ, and θ are also discussed. The presence of the spectra of nitrogen in the night sky is considered. An excellent bibliography of 49 references to previous work of other investigators is included.

Herman, R., L. Herman, J. Gauzit, "A Very Intense Infrared Radiation in the Light of the Night Sky", J. phys. radium, 6, 182, (1945).

The authors refer to their discovery of the infrared radiation in 1942. In the present paper they report an improved determination of the wavelength and found the value to be 10,400 A. They suggest that this could be the forbidden transition $^2P \rightarrow {}^2D$ of N I. The forbidden N I line $^2P \rightarrow {}^4S$ at 3466 A should also be observed in the spectrum of the night sky.

Herman, R., L. Herman, and J. Gauzit, "Infrared Spectrum of the Night Sky", Nature, 156, 114, (1945).

The authors report that they have photographed the infrared spectrum of the night sky employing a spectrograph with two prisms giving a dispersion of 2000 A/mm near 8000 A and of 3000 A/mm near 10,000 A. One feature of the spectrum was a very broad band at about 0.97μ and a line or band at about 1.03μ.

The broad band at about 0.97μ was interpreted as probably the water band at 0.94μ, while two possible origins were considered for the 1.03μ radiation: a. the (0,0) band of the first positive system of nitrogen whose wavelength head is 1.042μ; b. the forbidden doublet $^2P \rightarrow {}^2D$ of the N I atom (λ 10,410 A - λ 10,401 A).

The authors report from a private communication from an American colleague that the infrared N I doublet has been found to be permanently present in the spectrum of the night sky and that its intensity would exceed that of the green line of O I. It is stated that this confirmed a discovery by Gauzit [Compt. rend., 213, 695, (1941)] that nitrogen should be found essentially in the atomic state in the upper atmosphere. The following process was suggested as accounting for the (0,0) band of the first positive system corresponding to the B_0 - A_0 transition of the nitrogen molecule as well as the N I λ 10,410 A radiation.

$$\underbrace{\underset{6.14\ \mathrm{v}}{A_0} + \underset{3.56\ \mathrm{v}}{{}^2P}}_{9.70\ \mathrm{v}} \longrightarrow \underbrace{\underset{7.32\ \mathrm{V}}{B_0} + \underset{2.37\ \mathrm{v}}{{}^2D}}_{9.69\ \mathrm{v}}$$

Stebbins, Joel, A. E. Whitford, and P. Swings, "A Strong Infrared Radiation from Molecular Nitrogen in the Night Sky", Astrophys. J., 101, 39, (1945).

A new infrared radiation was detected in the night sky and the wavelength measurement was determined to be 10,440 ± 25 A. The two possibilities for the identification were: a. the forbidden $^2D \rightarrow {}^2P$ multiplet of N I; b. the (0, 0) band of the $B\ {}^3\Pi \rightarrow A\ {}^3\Sigma$ (first positive) group of N_2. The following table is included in the paper.

Lines of N I

$^4S \rightarrow {}^2D$	λ5197.8	E P 2.4 volts, transition probability 0.000021
	λ5200.1	E P 2.4 volts, transition probability 0.000014
$^4S \rightarrow {}^2P$	λ3466.4	E P 3.6 volts, transition probability 0.0094
$^2D \rightarrow {}^2P$	λ10,407.3	E P 3.6 volts, transition probability 0.21
	λ10,397.8	E P 3.6 volts, transition probability 0.25

The authors state that most observers agree that the radiation near λ5200 A is absent from the night sky, as expected from the transition probabilities in the table. The line λ3466 A is also considered absent, or hardly visible in, the night sky, although it is present in auroral spectra. It is also concluded that a [N I] emission cannot be a major contribution to the night sky emission near λ10,440 A.

The following is proposed, suggesting that the emission mechanism involves conversion of the energy of dissociation $D(N_2)$ into excitation in a three-body collision.

$$N + N + N_2 \rightarrow N_2 + N_2^*$$

The value of $D(N_2)$ is a little larger than the excitation energy of $B\ ^3\Pi$, $v' = 0$, but smaller than $B\ ^3\Pi$, $v' = 1$; only the bands arising from $B\ ^3\Pi$, $v' = 0$, would be excited, the (0,0) band being observable. The mechanism implies the presence of a large number of nitrogen atoms in the upper atmosphere. It is a plausible explanation if the value $D(N_2) = 7.38$ volts (a value of Herzberg and Sponer) is accepted.

Vegard, Lars and G. Kvifte, "Spectral Investigations of Aurorae and Twilight", Geofys. Publ., Oslo, 16, No. 7, (1945).

The authors in the present paper have included the following topics:

a. Results obtained from auroral spectrograms taken at Oslo during the years 1941-1943.

b. Tables giving wavelengths and possible interpretations of the lines and bands hitherto observed in the auroral luminescence.

c. The origin and height of emission of the yellow sodium line in twilight.

With reference to N I the authors give the following wavelength values from Edlen [Naturewiss., 26, 839, (1938)]:

$$\left.\begin{matrix} 5200.1 \\ 5197.8 \end{matrix}\right\} \quad ({}^4S_{3/2} \rightarrow {}^2D_{5/2,3/2})$$

$$3466.5 \quad ({}^4S_{3/2} \rightarrow {}^2P_{1/2,3/2})$$

The authors state that the doublet green lines cannot be identified with any of the known auroral lines and that they are probably too weak to be observed. The 3466.5 A line in the ultraviolet nearly coincides with a

fairly strong auroral line 3467.5 A. This line also nearly coincides with a band of the 2nd positive group and an O II line 3470.4 A. As a result it cannot be considered proved that the line N I ($^4S \rightarrow {}^2P$) is present in the auroral spectrum. It is regarded as a very probable interpretation since a number of other auroral lines may possibly be attributed to neutral or ionized nitrogen atoms. In Table VIII of the paper the authors have collected a list of N-lines (neutral and ionized atomic nitrogen) which coincide with observed auroral lines. The table contains 17 N I lines, 39 N II lines, and 11 N III lines.

1946

Bates, D. R. and H. S. W. Massey, "The Basic Reactions in the Upper Atmosphere", Phys. Roy. Soc. (London), A 187, 261, (1946).

This is an extensive and often quoted paper which discusses the properties of the upper atmosphere, and in particular the ionosphere and night sky emission. The following topics are discussed: a. mean composition, temperature and density; b. properties of the ionized layers--the D, E, F_1, and F_2 layers; c. production of atmospheric ionization, ionization potentials, ionized layer formation, the E, F_1 and F_2 layers; d. recombination, attachment, detachment and transfer reactions; e. equilibrium of atmospheric ionization; f. radiation of the night sky, origin of night sky emission. An extensive bibliography of about 100 references is included.

With reference to atomic nitrogen the dissociative recombination mechanism is given as a most promising action.

$$N_2 + h\nu \rightarrow N_2^+ + e^-$$

$$N_2 + e^- \rightarrow N' + N''$$

Cady, George H., "Origin of Nitrogen in Natural Gas", Science, 104, 341, (1946).

Reference is made to a paper by W. B. Lang [Science, 97, 329, (1943)] who had previously discussed the occurrence of nitrogen in natural gases and suggested that by analyzing suitable samples for nitrogen and the rare gases, argon, krypton, xenon, and neon, one could establish the probable source of the element. It was thought that if the relative proportions of nitrogen and argon in a natural gas sample were the same as in air, one might conclude that the nitrogen and argon had originally come from the atmosphere and were subsequently trapped within the earth. If the ratio of nitrogen to argon was much higher than that found in air, the nitrogen in the natural gas probably had been produced in the earth by chemical means.

Cady in the present paper calls attention to similar deductions and significant contributions to the literature by previous investigators. A table is included which shows wide variations in the (krypton, xenon)/argon ratio. It is suggested that the rare gases may have become partially separated from each other by natural processes. It is likewise possible that argon and nitrogen may have become separated from each other, and as a result occur in different proportions in different gases. Since there is no assurance that the inert gases in natural gas originally came from the atmosphere rather than from within the earth, Cady concludes that one cannot use the available analytical data as a basis regarding the origin of the nitrogen.

Dejardin, Georges and Jean Dufay, "The Ultraviolet Radiation of the Night Sky. II. Probable Origin of the Emission Spectrum", Ann. geophys., 2, 249, (1946).

This paper contains a revised list of all the emission lines and bands

in the spectrum of the night sky as previously tabulated by the authors [Cahiers phys., 12, 35, (1942)]. Reference is made to Barbier's measurements [Ann. geophys., 1, 224, (1945)]. The authors point out the necessity for testing statistically the proposed identifications of the lines and bands with known radiations. From this procedure it was possible to assign certain bands to the Vegard-Kaplan system of N_2, to the Lyman-Birge-Hopfield bands of N_2, and to the Herzberg, and Schumann-Runge system of O_2.

Gaydon, A. G., "The Determination of Dissociation Energies of the Birge-Sponer Extrapolation", Proc. Phys. Soc., (London), 58, 525, (1946).

This paper is a critical survey of the Birge-Sponer method of determining dissociation energies of diatomic molecules. The method consisted in the extrapolation of the vibrational energy levels to their convergence limit. The author states that when sufficient data are available for a large number of vibrational levels this graphical extrapolation, plotting the vibrational energy intervals $\Delta G(v + 1/2)$ against the vibrational quantum number v, may be expected to lead to fairly reliable results. It is pointed out that for a fair number of molecules accurate values of the dissociation energy have been obtained by other methods. These methods include (a) the observation of band spectra structure up to the convergence limit at which continuous absorption begins, (b) predissociation, and (c) thermochemical methods.

Reference is made to the dissociation energies of N_2, NO, CO, and CN discussed by Gaydon and Penney (1945). In Table 1 of the paper the author lists values of D_o (accurately determined dissociation energy) and D_{lin} (linearly estrapolated values) for the ground state of molecules with non-ionic bonding. The values for N_2, NO, CO, H_2, CN and O_2 are

included here.

Molecule	D_o	D_{lin}	D_o/D_{lin}
H_2	4.478	4.55	0.99
CO	11.11	11.2	0.99
NO	6.49	7.6	0.85
CN	7.6	9.9	0.77
O_2	5.084	6.3	0.81
N_2	9.764	11.8	0.83

Herman, R. and A. G. Gaydon, "Band Systems of the Neutral Nitrogen Molecule", J. phys. radium, 7, 121, (1946).

The experimental study and identification of new band systems in the visible emission and ultraviolet spectra of molecular nitrogen are discussed. Three tables are included which compare identifications by both Gaydon and Herman.

Herman, Renee and Louis Herman, "Spectra of Nitrogen in an Atmosphere of Xenon." J. phys. radium, 7, 203, (1946).

This is an excellent and thorough discussion of the first investigation by the authors on the spectrum of a discharge by exciting nitrogen under low pressure in an atmosphere of xenon. The diagram of the discharge tube is included, and a description of its preparation and the purification of the gases are given. The pyrex tube had a diameter of 35 mm and a length of 150 cm with a fused quartz window at one end. It was filled with xenon at a pressure of 10 mm Hg. After the addition of a trace of nitrogen an electric discharge was passed through the tube.

The spectrum was observed from the infrared to $\lambda 2000$ A. The first positive system of N_2 bands in the infrared was observed. It the visible and ultraviolet to 2800 A the second positive system and the Vegard-Kaplan bands were observed, while below 2800 A only the latter bands appeared. The forbidden line of N I at $\lambda 3466$ A ($^4S \rightarrow {}^2P$) was also emitted. A bibliography of eleven select references to previous work by other investigators is included.

Herzberg, Gerhard, "On the Electronic Structure of the Nitrogen Molecule", Phys. Rev., 69, 362, (1946).

It is shown in this paper that the Lyman-Birge-Hopfield bands of nitrogen represent a forbidden $^1\Pi_g - {}^1\Sigma_g^+$ transition. The author gives a revised electronic energy level diagram of N_2. A revision of Gaydon and Worley's table of the singlet states of the nitrogen molecule is included. Considerable difficulty in the interpretation of the electronic states of N_2 by electron configurations has been removed on the basis of the revised types presented in this discussion.

Hopfield, J. J., "Ultraviolet Absorption Spectrum of Air in the Region $\lambda\lambda$ 600 - 2000", Astrophys. J., 104, 208, (1946).

The laboratory study of the absorption spectrum of air is published in the present paper to serve as a guide to the ultraviolet spectrum of the sun from high altitudes. The data of the absorption spectrum of air in the region $\lambda\lambda 600$-2000 A was obtained with a vacuum-grating spectrograph at the University of California about twenty years prior to the present paper. A brief description of the spectrograph is given. The chamber of the spectrograph served as a 100-cm absorption cell holding the sample of air. The pressures and equivalent length of air column could be varied from 100 cm to values as low as 0.0019 cm. The equivalent air

thickness values were comparable to the absorption of the air for sunlight at altitudes of from 72 km and to more than 120 km.

Plate III in the paper shows an excellent absorption spectrum of the air. It was assembled from spectra taken with different pressures of air for the spectral region $\lambda\lambda$ 600-2000 A. The equivalent thickness of air is calculated from the following expression,

$$\text{Air thickness} = \frac{P}{76} \times 100 \text{ cm}$$

where P is the air pressure in the spectrograph in cm of Hg, and the length of the absorption cell is 100 cm. The following table appears to the right of the various spectra shown in Plate III.

Spectrum number	P in spectrograph cm Hg	Equivalent air thickness cm at 1 atm.	Equivalent height above Earth km
1	0.0015	0.0019	---
2	0.0035	0.0046	---
3	0.016	0.021	---
4	0.03	0.039	---
5	0.06	0.079	---
6	0.1	0.131	128
7	0.4	0.526	115
8	0.8	1.05	109
9	1.6	2.11	103
10	3.2	4.21	96
11	10.0	13.16	86
12	20.0	26.3	81
13	76.0	100.0	72
14	76 cm O_2	---	---

The following inferences are made. a. The atmosphere at high altitudes is much more transparent in the $\lambda\lambda 1000$-1300 region than in $\lambda\lambda 1300$-1700, the latter being the region for the convergence limit of continuous absorption in the Schumann-Runge bands of O_2. b. At the height of 86 km one could extend the solar spectrum to $\lambda 1800$ A. c. At the height of 96 km the solar spectrum might be observable to $\lambda 1750$ A and a second region $\lambda\lambda 1100$-1200 A. d. As one approaches 128 km the first region of transparency lengthens, and the second one broadens and forms open windows to the light of the sun and stars.

Kaplan, Joseph, "Afterglows and the Upper Atmosphere", Phys. Rev., 70, 448, (1946).

This is an abstract of a paper read at the 273rd regular meeting of the American Physical Society held at University of California, Berkeley, 12-13 July 1946. It is stated that nearly all of the modifications of molecular and atomic oxygen and nitrogen that are present in the earth's upper atmosphere have been studied in afterglow laboratory experiments. Attention is called to some recent conclusive results regarding the roles played by atomic nitrogen and nitrogen molecular ions in auroral afterglows and in the upper atmosphere.

Kastler, Alfred, "Report on the Investigations of Optical Phenomena of the High Atmosphere during the Period 1940-1945", Ann. geophys., 2, 315, (1946).

This is an excellent survey and review of solar radiation, auroras, night sky radiations, constitution of the high atmosphere, correlation of solar activity, and optics of the upper atmosphere obtained from laboratory experiments and theoretical deductions. Atomic nitrogen is considered under the topic of the polar aurora. An excellent and extensive bibliography of 118 references is included.

Valatin, J. G., "On the Dissociation Energies of CO, N_2, NO, and CN", J. Chem. Phys., 14, 568, (1946).

In this letter to the editor reference is made to the work of Gaydon and Penney (1945) who determined the dissociation energies of CO, N_2, NO, and CN by a systematic application of the non-crossing rule of the energy eigenvalue curves of the two-center problem of the potential curves of the molecule. Reference is also made to the several papers by R. Schmid and L. Gero (1937, 1938, 1939, 1943, 1944). The latter workers have pointed out several times that the non-crossing rule cannot be applied to the correlation of molecular terms with the atomic term combinations. In Table I of the present paper the following data for N_2 and NO are given,

Molecular ground state	Dissociation products	Bond Energy cm^{-1}	Lowest atomic term combination	Dissociation energy cm^{-1}
N_2 $X\ ^1\Sigma_g^+$	$N(^2D) + N(^2D)$	78, 750	$N(^4S) + N(^4S)$	40, 350
NO $X\ ^2\Pi$	$N(^2D) + O(^3P)$	53, 800	$N(^4S) + O(^3P)$	34, 600

The author points out that the bond energies are to be counted from the atomic term combination corresponding to the dissociation of the molecular state. Thermochemical dissociation energies are the lower values counted from the lowest atomic term combination.

Vegard, Lars, "Spectroscopy in the Higher Atmosphere", Physica, 12, 606, (1946).

This is a general paper on the physics of the upper atmosphere. Above 70 km the density is very small and decreases with altitude, and the matter

is exposed directly to various solar radiations which rapidly diminish downwards towards the earth's surface. The composition and physical properties of the upper atmosphere will differ essentially from the conditions observed in the lower part.

The following are listed as most important phenomena which takes place in the higher atmosphere and which may be observed on the surface of the earth.

a. The aurora borealis.

b. The night sky luminescence.

c. The zodiacal light.

d. Twilight luminescence.

e. Meteors.

f. The state of ionization and electric conductivity and its influence on the the propagation of electro-magnetic waves.

The author gives a brief history of his investigations in collaboration with Tönsberg, Harang, and Kvifte on the spectroscopy of the upper atmosphere and the study of the aurora. The greatest number of auroral spectrograms were obtained in northern Norway; from 1911-1912 at Bosekop, from 1922-1926 at the Geophysical Institute at Tromso, and after 1929 at the Auroral Observatory.

The paper includes the following table which characterizes the auroral spectrum by the appearance of the various band system originating from nitrogen.

Name of the band System	Electronic Transition
Negative Group (N. G.)	$N_2^+ \ (B\ ^3\Sigma - X\ ^2\Sigma)$
2nd Postive Group (2 P. G.)	$N_2\ (C\ ^3\Pi - B\ ^3\Pi)$
1st Postive Group (1 P. G.)	$N_2\ (B\ ^3\Pi - A\ ^3\Sigma)$
The ϵ-system (Vegard-Kaplan bands)	$N_2\ (A\ ^3\Sigma - X\ ^1\Sigma)$

The negative bands are strong in blue and violet, the 2nd Postive in ultraviolet, the 1st Positive in red and infrared, and the ϵ - system is very weak in the auroras. The following lines of O I were also observed.

Green line O I ($^1D_2 \rightarrow {}^1S_0$) λ 5577.345 A

Strongest red line O I ($^3P_2 \rightarrow {}^1D_2$) λ 6300.300 A

Weaker red line O I ($^3P_1 \rightarrow {}^1D_2$) λ 6364.0 A

The author states that in addition to the strong nitrogen bands and these O I lines, under favorable conditions by long exposure and temperature regulation of the instruments a number of weak lines are obtained. During the period 1940-1943 Vegard and his co-workers were able to measure the earlier known lines with great accuracy and showed 47 new lines, the wavelengths of which were determined with fair accuracy. An extensive table is included which lists all auroral lines and bands as yet detected and measured.

With reference to atomic nitrogen it is stated that the appearance of strong nitrogen bands and the absence of oxygen bands indicates that the degree of dissociation in the auroral region is much greater for oxygen than for nitrogen, and that this would account for the weakness of the atomic nitrogen lines. The following lines of neutral atomic nitrogen and the metastable ground state are observable: λ3466.5 A of N I ($^4S_{3/2} \rightarrow {}^2P_{1/2,3/2}$), $\lambda\lambda$5200 and 5197.8 A of N I ($^4S_{3/2} \rightarrow {}^2D_{5/2,3/2}$). The author states that the first of these lines (3466.5 A) may possibly be identical with the auroral line 3467.5, but that the doublet with average wavelength 5199 A cannot be identified with the auroral line 5202.9 since the difference in wavelength is greater than possible error.

An additional remark is made by A. Kastler (Paris) that the discovery of the forbidden lines of atomic nitrogen in the spectrum of the auroras of low latitude [Bernard, Ann. astrophys., L, 1, (1941); J. Dufay, J. Gauzit, and Tcheng Mao-Lin, Cahiers phys., 1, 1, (1941); P. Gotz, Naturwiss., 29, 690, (1941); J. Dufay, Ann. astrophys., 6, 81, (1943)] and the identification of bands of molecular oxygen in the spectrum of the night sky indicate the presence of both atomic oxygen and nitrogen in the high atmosphere.

Verdier, Edgar T., "The Mean Life of Active Nitrogen", Compt. rend., 222, 731-733, (1946).

The mean lifetime for the emission of ultraviolet radiation from the gas in the vicinity of the anode during the electrolysis of azide solutions has been reported previously by R. Audubert and Charles Racz [Bull. Soc. Chim., 7, 907-914, (1940); Compt. rend., 210, 217-219, (1940)]. The slow electrolysis of aqueous azide solutions is accompanied by ultraviolet radiation which is independent of the cation. The electronic spectrum shows that the molecular nitrogen passes through metastable states. Spectral analysis has shown that these states differ from the active nitrogen described by Lord Rayleigh. The mean lifetime of the active nitrogen prepared from azides was determined to be 4.7×10^{-2} sec at a pressure of 2 cm. The lifetime is increased by reducing the pressure; at a pressure of one atmosphere of air the value was 2.5×10^{-3} sec, while in one atmosphere of nitrogen the lifetime was increased to 6.0×10^{-3} sec.

1947

Barbier, Daniel, "Spectrophotometric Studies of the Spectrum of the Night Sky ($\lambda\lambda$ 4600 - 3100 Å)", Compt. rend, 224, 635, (1947).

In this note Barbier states that the observed contour of the Herzberg oxygen bands indicated a temperature of -50^{o} to 100^{o} C. The oxygen bands originate at a 350-km altitude as indicated from spectra taken at 10^{o} and 80^{o} from the zenith. The altitude of the Vegard-Kaplan nitrogen bands was 900 km.

Bernard, Rene, "Wavelength of the Atomic Nitrogen Line N I ($^4S \longrightarrow {}^2P$) in the Spectrum of the Aurora Borealis", Ann. geophys., 3, 63, (1947).

The author has reported from microphotometer tracings of a low-dispersion spectrogram of the aurora borealis and a comparison spectra of helium-nitrogen that the value of the wavelength of the N I line was determined to be 3466.5 A. Reference is made to the value obtained by Kaplan [Phys. Rev., 54, 541, (1938)] who obtained 3466.3 A for the line. The agreement is satisfactory. It confirms the identification of the line in the spectrum of the aurora with the line $^4S \longrightarrow {}^2P$ of N I.

Fast, J. D., "The Dissociation of Nitrogen in the Welding Arc", Philips Research Reports, 2, 382, (1947).

In this research paper the author has computed the dissociation of molecular nitrogen on the basis of spectroscopic data for the temperature range 5000 to $10,000^{o}$K and for three different values of the dissociation energy: 7.383, 8.573, and 9.764 electron volts. The following topics are thoroughly discussed in the report.

a. The temperature of the welding arc.

b. Statistical-mechanical basis of the calculations.

c. The partition function of atomic nitrogen.

d. The partition function of molecular nitrogen.

e. The "exact" evaluation of the partition function for molecular nitrogen.

f. The dissociation of N_2 in the temperature range 5000-10,000°K.

g. Discussion of the results.

Many valuable tables of data are included in the paper. For example Table VII gives the reaction constant, K_p, for the reaction

$$N_2 \rightleftarrows 2N,$$

$$\left[\quad K_p = \frac{p_N^2}{p_{N^2}} \quad \right]$$

using the three different values of the dissociation energy for the temperatures, 1800, 2750, 5000, 6000, 7000, 8000, 9000, and 10,000°K. Table VIII gives the degree of dissociation, α , for N_2 at a total pressure of one atmosphere for the three dissociation energy values and the above temperatures. The author states that the value

$$D(N_2) = 9.764 \text{ ev}$$

of Gaydon and Penny (1945) is probably the correct one. An excellent bibliography of 21 references to the journal literature is included.

Götz, F. W. Paul, "The Spectrum of the Northern Lights of 17 April 1947", Experimentia, 3, 185, (1947).

The author reports the observation of the forbidden line 5199 A of atomic nitrogen in the spectrum of the aurora of 17 April 1947. This again confirms the long duration of this excitation.

Meyerott, Roland E., "Validity of the Franck-Condon Principle in Collisions of the Second Kind", Phys. Rev., 71, 553, (1947).

The author has discussed in this letter to the editor the application

of the principle of resonance to collisions of the second kind between an atom and a molecule or between two molecules. It is stated that collisions of the second kind between two molecules are more restricted since the Franck-Condon principle must hold for each of the colliding molecules. For collisions between molecular states in active nitrogen the excitation is accounted for in detail by applying the Franck-Condon principle to the forbidden transitions

$$A\ {}^3\Sigma_u \rightarrow X\ {}^1\Sigma_g$$

$$a\ {}^1\Pi_g \rightarrow X\ {}^1\Sigma_g$$

and

$$a\ {}^1\Pi_g \rightarrow A\ {}^3\Sigma_u$$

in N_2. It is concluded that there are no mechanisms for converting an excess energy of the order of volts into vibrational or transitional energy of the colliding molecules.

1948

Barbier, Daniel, "Excitation of Forbidden Lines in Nebulae, Novae, and Polar Auroras by Electron Collisions", Ann. astrophys., 11, 193, (1948).

This is an extensive theoretical discussion of the forbidden transitions in the neutral atomic oxygen and nitrogen spectra observed in nebulae, novae, and auroras. The forbidden lines result from transitions from metastable states to the ground states of the atoms. The excitation of the atoms is attributed to their collisions with free electrons which come from atoms and molecules in the atmosphere by primary ionizing particles of high energy.

Bates, D. R., H. S. W. Massey, and R. W. B. Pearse, "The Aurora", Emission Spectra of the Night Sky and Aurora (Asupices of the Gassiot Committee of the Royal Society in London). The Physical Society, p. 97, (1948).

By way of introduction the authors point out the uncertainties and fifficulties which arise in the identification of the auroral bands and lines. Interpretations necessarily must be made with caution and proper attention paid to their general plausibility. Since the study of the auroral spectra has for the most part been carried out by the Norwegian investigators, the summary by Vegard and Kvifte (1945) is taken as the basis for the discussion in the present paper.

With reference to atomic nitrogen Vegard and Kvifte suggested various lines from the spectra of N I, N II, and N III to account for the many wavelengths measured. Of these, seventeen lines were listed for N I, thirty nine for N II, and eleven for N III. The authors of the present paper state that the identifications of the allowed atomic lines are still far from convincing. The theories of Vegard and of Mitra and Ghosh for the production of the observed auroral emissions are discussed.

It is pointed out that any final theory must explain the absent emissions: how certain emissions occur but certain others are absent or very weak. Reference is made to Nicolet (1942) who showed that even if the rate of excitation of the relevant metastable states are comparable to the forbidden lines of O I, the N I lines would still be relatively weak. The following table is included which explains the reason for the relatively weak lines of N I.

Transition	Wavelength (A)	Initial J Value	Transition probability (per sec)
$^4S \rightarrow {}^2D$	5200	3/2	2.1×10^{-5}
		5/2	3.2×10^{-5}
$^4S \rightarrow {}^2P$	3466	1/2	3.6×10^{-3}
		3/2	9.0×10^{-3}
$^2D \rightarrow {}^2P$	10,400	1/2	2.5×10^{-1}
		3/2	2.6×10^{-1}

The transition probability from the ^2D state is so low that collision de-activation could well reduce the intensity of λ 5200 A very greatly, while the comparatively rapid depopulation of the ^2P state by emission of λ 10,400 A would explain the low intensity of λ 3466 A. As a result no anomaly is presented.

Bates, D. R. and M. J. Seaton, "The Quantal Theory of Continuous Absorption of Radiation by Various Atoms in Their Ground States", Mon. Not. Roy. Astron. Soc., 109, 698-704, (1948).

In this paper Bates and Seaton have calculated the absorption cross-section for atomic nitrogen. The exchange wave functions and both the dipole moment and dipole velocity formulas were used. Reference is made to the earlier calculations on atomic nitrogen by Brown, Bartlett, and Dunn [Phys. Rev., 44, 296-299, (1933)] and Hartree and Hartree [Proc. Roy. Soc., A 193, 299-304, (1943)]. The following continuous radiative absorption cross-section values are given for atomic nitrogen:

value from dipole moment formula = 10.2×10^{-18} cm^2
value from dipole velocity formula = 7.7×10^{-18} cm^2
recommended value = 9.0×10^{-18} cm^2

Bernard, Rene, "The Wavelength of the N I Line ($^4S \rightarrow {}^2P$) of Atomic Nitrogen in the Spectra of the Aurora Borealis", Emission Spectra of the Night Sky and Aurora, (Auspices of the Gassiot Committee of the Royal Society in London), The Physical Society, p. 91, (1948).

The wavelength of the N I line was calculated to be 3466.5 A. The observed experimental value is 3466.3 A. The author concludes that the presence of the radiation from N I ($^4S \rightarrow {}^2P$) in the spectra of the aurora borealis is now definitely established.

Hartree, D. R. and W. Hartree, "Self-Consistent Field, with Exchange, for Nitrogen and Sodium", Proc. Roy. Soc. (London), A 193, 299-304, (1948).

This paper is a report of the normal electron configuration of neutral nitrogen (N^0) and that of N^-. Wave functions for each were calculated by the method of the self-consistent field with exchange. The normal electron configuration of neutral nitrogen is $1s^2\ 2s^2\ 2p^3$ giving terms ^4S, ^2D, ^2P in that order, ^4S being deepest. The configuration for N^- is $1s^2\ 2s^2\ 2p^4$ giving ^3P, ^1D, ^1S.

The normalized wave functions for neutral N are tabulated in Table 1 of the paper. The following energies are given in Table 3 for the various states of N^0 and N^-.

		Calculated Total Energy of 2s 2p shell
N^{o}	^{4}S	-9.651
	^{2}D	-9.559
	^{2}P	-9.496
N^{-}	^{3}P	-9.587
	^{1}D	-9.533
	^{1}S	-9.444

Herman, L. and R. Herman, "Mechanism of the Emission Spectrum of Active Nitrogen", Nature, 161, 1018-1019, (1948).

Reference is made to Mitra's theory of the nitrogen afterglow and also to the later studies of Lord Rayleigh, who suggested the recombination between N_2^+ ions with electrons. In the present note the authors report their attempt to investigate the effect of temperature on the afterglow. The following topics are considered:

a. first positive system,

b. second positive and second negative systems,

c. goldstein bands,

d. green system.

The results of the present investigation appear to show that Mitra's theory of 1945 is unable to explain all the features of active nitrogen. It is stated that diatomic nitrogen is similar to an inert gas that permits many reactions between atoms, ions, and electrons.

Herzberg, G. and L. Herzberg, "Production of Nitrogen Atoms in the Upper Atmosphere", Nature, 161, 283, (1948).

The authors state that during recent years evidence has accumulated

that nitrogen is at least partially dissociated in the upper atmosphere. The precise process causing the dissociation has not been established. Reference is made to the suggestion of Ta-You Wu [Phys. Rev., 66, 65, (1944)] who suggested that nitrogen is only dissociated by extremely short wavelengths in the extreme ultraviolet beyond λ500 A.

The authors report that they were able to confirm a breaking-off in nitrogen excited at low pressure in a high frequency electrodeless discharge. The break-off above the level $v' = 6$ in the Lyman-Birge-Hopfield (a - X) bands of nitrogen had been observed by Herman [Compt. rend., 217, 141, (1943); Ann. phys., (11), 20, 241, (1945)].

In the study reported in this paper the appearance of the spectra seemed to indicate a definite predissociation of the molecule. The predissociation limit is between the levels $v' = 6$ and 7 of the ($a\ ^1\Pi_g$) state at an energy of approximately 98 ev. This energy value is in close agreement with that necessary to dissociate N_2 into N (^{4}S) and N (^{2}D), assuming $D(N_2) = 7.38$ ev. It is stated that the (a - X) bands are the only absorption bands of N_2 above 1150 A, and that the absorption is comparatively weak because the bands represent a forbidden transition.

The authors state that the $v'' = 0$ progression was observed in the absorption from 0 - 0 to the 9 - 0 band. The 7 - 0, 8 - 0 and 9 - 0 bands have the wavelengths, respectively, of 1249.3, 1226.6, and 1205.3 A. Absorption of solar radiation of these wavelengths was considered to lead to the production of nitrogen atoms in the upper atmosphere. This mechanism was considered to occur over a very considerable range of heights since absorption by oxygen molecules in the spectral region 1150 - 1250 A is comparatively weak. Thus it is possible to account for the presence of nitrogen atoms at comparatively low heights and for the presence of nitrogen molecules at much greater heights, as observed in auroras.

Kaplan, Joseph, "Active Nitrogen", Phys. Rev., 73, 494, (1948).

In this paper Kaplan considers Mitra's (1943) hypothesis of the nature of active nitrogen and the mode of excitation of the light of the night sky. According to this hypothesis a three-body collision involving a molecular nitrogen ion in the X' state, an electron, and an excited nitrogen molecule react to yield two excited molecules.

$$N_2^+ \cdot (X') + e^- + N_2 \longrightarrow N_2 \text{ (B - state)} + N_2 \text{ (A - state)} \quad (a)$$

The energy of the A-state, v = 0, is 6.14 volts, while that in the B-state, v = 11, is 9.43 volts. Since the ionization potential of nitrogen is 15.58 volts, enough energy is available to account for these excitations.

Kaplan gives the following as the two most important reactions occurring in the auroral afterglow and perhaps in the Lewis-Kaplan glow.

$$N_2^+ + e^- \longrightarrow N' + N'' \qquad (b)$$

$$N' + e^- \longrightarrow N + e^- \qquad (c)$$

In reaction (b) an electron recombines with a positive ion in the N_2^+ (X') level in a dissociative process giving two nitrogen atoms in the metastable ^2P state. Assuming 7.38 volts for the heat of dissociation for a neutral nitrogen molecule, the amount of energy required for the production of two metastable nitrogen atoms in the ^2P state would be 14.5 volts, the energy of the ^2P level being 3.56 volts.

$$7.38 + 3.56 + 3.56 = 14.5$$

Reaction (b) is therefore energetically possible.

Meinel, A. B., "The Near-Infrared Spectrum of the Night Sky and Aurora", Publ. Astron. Soc., Pacific, 60, 373, (1948).

This is a report of a preliminary survey of the near-infrared spectrum of the night sky and of a low latitude aurora. A detailed account is given of the instrumentation employed in the present investigation. Table I in the paper is a list of wavelengths in night sky and aurora spectra obtained from five night sky plates and from one auroral plate. The following two lines are included for N I: $\lambda 8684$ A ($3p\ ^4D - 3s\ ^4P$) and $\lambda 8714$ A ($3p\ ^4D - 3s\ ^4P$).

Mitra, S. K., "Active Nitrogen", Phys., Rev., 74, 1637, (1948).

The author in the present paper has examined the remark made by Kaplan [Phys. Rev., 73, 494, (1948)] that Mitra's contribution to the problem of active nitrogen will play a part in the explanation of the mode of excitation of the auroral afterglow, yet that the principal reactions occuring are not those proposed by Mitra. Mitra's theory of active nitrogen first considers the nature of active nitrogen, and secondly the nature and role of the conditioned wall of the airglow vessel which prevents the destruction of the active substance.

It is pointed out that contrary to Kaplan's view, the strengthening of the Vegard-Kaplan bands originating in v' = 11 in the later stage of the auroral afterglow does not contradict the following reaction which Mitra proposed,

$$N_2^+ (X') + e^- + N_2 \longrightarrow N_2 (B) + N_2 (A),$$

in which the N_2 (B) molecule emits the first positive bands by transition $B \longrightarrow A$. The N_2 (A) molecules are considered to be in metastable state with long lives. It is also pointed out that the persistence of the first

negative bands throughout the entire duration of the auroral afterglow indicates that nitrogen ions in the N_2^+ $(A' \, ^2\Sigma)$ state have long life. The author concludes that Kaplan's discovery that N_2^+ (X') ions persist in the auroral afterglow throughout its duration, and also that Kaplan's alternative reactions start with these ions, supports Mitra's hypothesis that active nitrogen is nitrogen ions in the N_2^+ (X') state.

Nicholls, R. W., "Excitation Processes in Molecular Nitrogen", Nature, 162, 231-232, (1948).

The author has suggested an excitation process in molecular nitrogen which is claimed to account for the observed experimental results without violating either the selection rules or the Franck-Condon principle. The process involves excitation by collision between ground state molecules and electrons in the population of the singlet-levels at $^1\Pi$ and b. The latter is a group of eight levels between 12.5 and 14 volts.

A summarizing table is included in the paper giving energy levels, band systems, and appearance potentials. This mechanism may have an important bearing on auroral excitations.

Nicolet, Marcel, "Deductions Regarding the State of the High Atmosphere", Emission Spectra of the Night Sky and Aurora, (Auspices of the Gassiot Committee of the Royal Society in London), The Physical Society, p. 36, (1948).

With reference to the spectral emission of the night sky the author refers to the forbidden transitions λλ5577, 6300, and 6364 A of O I, some bands of the Vegard-Kaplan and the First Positive N_2 systems, the Herzberg O_2 system, and finally the Na I radiation. Nicolet states that there is absence, or at least weak intensity, of the forbidden

radiations of N I in the night sky but which are observed with certainty in the auroral spectrum.

It is stated that for the neutral nitrogen atom (N I) the forbidden transition $^4S \rightarrow {}^2P$ (λ3466.5 A) has not been observed in the night sky. The double radiation λλ5198 - 5200 A corresponds to the transition $^2D \rightarrow {}^4S$ of N I, while the infrared radiations of the transition $^2D \rightarrow {}^2P$ are situated in a spectral range where observations show strong emission; however the author concludes that the essential contribution to the night sky luminescence cannot be due to atomic nitrogen.

The author discusses the following processes resulting from photodissociation and photoionization which are applicable to atomic nitrogen.

$$N_2O + h\nu \quad (\lambda < 2140 \pm 130 \text{ A}) \rightarrow NO\,(^2\Pi) + N\,(^2D) \qquad \text{(a)}$$

$$N + O_2 + M \rightarrow NO_2 + M + h\nu \rightarrow NO + O + M \qquad \text{(b)}$$

$$N + N + M \rightarrow N_2 + M \qquad \text{(c)}$$

$$N + O + M \rightarrow NO + M \qquad \text{(d)}$$

$$N^+ + N \rightarrow N_2^+ + h\nu \qquad \text{(e)}$$

$$N + O^- \rightarrow NO + e^- \qquad \text{(f)}$$

$$NO + h\nu \quad (\lambda < 1312 \pm 15 \text{ A}) \rightarrow NO^+ + e^- \qquad \text{(g)}$$

$$NO^+ + h\nu \quad (\lambda < 1312 \pm 15 \text{ A}) \rightarrow N + O^+ \qquad \text{(h)}$$

It is concluded that the constituents, O, N, and N_2 are found in the whole of the upper atmosphere and characterize the F_1 and F_2 regions.

From the following equations the author deduces the intensity ratio of the radiations λλ 3466.6 and 5200 A, which is found to depend on the ratio of atoms in equilibrium in the ^2P and ^2D states.

$$I_{ki} = N_k A_{ki} h\nu_{ki} \qquad \text{(i)}$$

$$N_k = N_o \quad (\rightarrow k) / \left\{ \sum a_{kj} + \sum A_{kj} \right\} \qquad \text{(j)}$$

$$I_{ki} = N_o \quad (\rightarrow k) \quad A_{ki} \; h\nu_{ki} / \left\{ \sum a_{kj} + \sum A_{kj} \right\} \qquad \text{(k)}$$

where I_{ki} is the intensity of radiation, N_k is the number of atoms in the upper state k, A_{ki} is the probability of the transition, and a_{kj} is the probability of collision de-activation. It is concluded that the vertical distribution of the emission of the forbidden transitions in the upper atmosphere is related to the vertical distribution of de-activiation mechanisms provided that it depends on the excitation processes.

Pauling, Linus, "The Electronic Structure of Excited States of Simple Molecules", Z. Naturforsch., 3a, 438, (1948).

In this paper Pauling has discussed the electronic structure of excited states of diatomic molecules in terms of valence bonds. The following data are given for N_2 and N_2^+ in Table II in the paper.

		A_o e.v.	Bond Structure
N_2	$X\ {}^1\Sigma_g^+$	0	$:N \equiv N:$
	$A\ {}^3\Sigma_u^+$	6.17	$:\dot{N} = \dot{N}:$
	$B\ {}^3\Pi_g$	7.34	$\cdot N \overset{\cdots}{=} N:$
	$a\ {}^1\Pi_u$	8.53	$\cdot N \overset{\cdots}{=} N:$
	$C\ {}^3\Pi_u$	11.01	$\cdot N \overset{\cdots}{=} N:$
N_2^+	$X\ {}^2\Sigma_g^+$	0	$\cdot N \equiv N:$
	$B\ {}^2\Sigma_u^+$	3.18	$\cdot N \equiv N:$

The normal state of the N_2 molecule is the triple-bonded state, $X\ ^1\Sigma_g^+$. The transfer of one of the s electrons of the nitrogen atom to a p orbital would require considerable energy. The molecule may be excited by destroying one of the bonds constituting the triple bond by unpairing two π electrons in the molecule, producing a $^3\Sigma_u^+$ state. If an s electron of one of the nitrogen atoms is promoted to the p orbital, a double bond and a three-electron bond may be formed between the nitrogen atoms. This structure gives rise to four states $^3\Pi_g$, $^3\Pi_u$, $^1\Pi_g$, and $^1\Pi_u$. The states for which the internuclear distance is known are listed in the table.

The topic of dissociation energies and bond energies is discussed in the paper. In regard to the values of $D(N_2)$ for nitrogen those of 7.383, 8.573, and 9.764 ev are most likely. The value of the dissociation energy obtained by extrapolation, $D_{extrap.}$, diminished by the valence correction for two nitrogen atoms is 8.46 ev (11.80 - 2 x 1.67 ev; 1.67 ev above the normal state, ^4S). This supports the value 8.573 ev for $D(N_2)$.

Setlow, R. B., "High Energy States of N_2^+ and N_2^*", Phys. Rev., 74, 153, (1948).

Reference is made to the discovery of the intense bands of the N_2^+ spectrum in the region λ 1860 A by Birge and Hopfield (1928), and their identification by Watson and Koontz (1934). In the present paper Setlow has analyzed the rotational structure of the C-X bands of N_2^+. This gives evidence of the validity of the Franck-Condon principle. Potential energy curves for the C and X states of N_2^+ are shown.

The Birge and Hopfield bands had been tentatively identified by them as a transition from an upper electronic state b' to the ground state of N_2 and designated $X\ ^1\Sigma_g^+$. Watson and Koontz (1934) obtained

1.147 cm^{-1} for the value of B'. The author in the present study states that there are two groups of strong lines arising from transitions v = 1 of b' to the ground state. The centers are found to be about 40 cm^{-1} and 120 cm^{-1} from the band heads. The author concludes from his investigation that the Birge and Hopfield c state is in reality the v = 1 level of the b' state. Evidence is also given that the c state of Worley (1943) is identical with the p' state of Gaydon.

Swings, P., "The Spectra of the Night Sky and of the Aurorae", Publ. Astron. Soc., Pacific, 60, 18, (1948).

The author states that information regarding the chemical composition and physical state of the earth's upper atmosphere may be obtained from spectra of the radiations emitted by the night sky, the aurorae, and by the sky at twilight or dawn, by studies of meteors, by the measurement of the reflection of radio waves from the ionosphere, by measurements from rockets, by observation of noctilucent clouds, by studies of magnetic fluctuations, refraction of sound waves, and the ozone layer. Also a vast amount of new observational and theoretical data on phenomena of the night sky, of aurora, and of twilight has been accumulated recently, especially in France, Norway, England, and Belgium. The present paper deals with several important conclusions and makes suggestions for further work. While there are many unidentified features in the spectra of the night sky and aurora the following are listed as satisfactorily identified.

Night Sky: (0, 0) band of 1st positive system of N_2 (λ 10440 A); O I (green and red lines); Na I (d-line); Vegard-Kaplan system of nitrogen; Herzberg system of O_2; a few bands of the first positive system of N_2 in the red region.

Aurorae: O I (green and red lines); N I ($\lambda\lambda$3466 and 5200 A); negative system of N_2^+; 1st and 2nd positive systems of N_2; Vegard-Kaplan system of N_2; occasionally lines of Na, H, and probably He I; probably O_2^+ ("second green line"); possibly NO. The above are those listed in Vegard's (1945) tables.

The author states that there is no doubt that at the most frequent heights of aurorae (90 to 120 km) de-excitation phenomena are of utmost importance. The ultraviolet N I line (average lifetime 100 seconds) is an example. However for the λ 5200 line of N I in the high aurora (average lifetime of upper level ^2D when unperturbed, eight hours) the de-activation phenomena do not play any major role. The line λ 5200 was observed by Götz to be still quite strong one hour after cessation of the aurora.

The presence of nitrogen atoms is required for the following recombination mechanisms for the interpretation of the (0,0) band of the first positive group of N_2 at λ 10440 A.

$$N + N + N_2 \longrightarrow N_2 + N_2^*$$

OR

$$N + N \longrightarrow N_2^*$$

Swings states that the general result of the studies on the night sky and aurorae leads to the conclusion that nitrogen atoms are present in the upper atmosphere. From an observation of the N I lines in aurorae the N I atoms have very high abundances, comparable to or higher than the oxygen atoms. It is possible that N I atoms are formed by predissociation of N_2 molecules in the region of λ 1400A, as postulated by Herzberg. Nicolet (1945) considers the formation of NO molecules and N I atoms without photodissociation of N_2 molecules. The author

states that it is certain that the usually adopted composition of the upper atmosphere, oxygen atoms and N_2 molecules, is false. Nitrogen atoms should certainly be added.

Worley, R. Edwin, "A Search for Spectral Absorption in Active Nitrogen", J. Chem. Phys., 16, 533-536, (1948).

An attempt was made to test for absorption by the small fraction of metastable molecules in the A $^3\Sigma$ state of the afterglow of active nitrogen and to test for absorption by ions in the X $^2\Sigma$ state. The four spectral ranges studied were (a) visible $\lambda\lambda$ 4550 to 6800 A, (b) near infrared $\lambda\lambda$ 8600 to 10950 A, (c) red $\lambda\lambda$ 6500 to 8900 A, and (d) near ultraviolet $\lambda\lambda$ 3600 to 4200 A. The optical path was 13 meters (10 traversals, 14 reflections).

No absorption due to active nitrogen was observed in any of the spectral ranges photographed. A supplementary test of the absorption system was made with dry air and then dry oxygen at atmospheric pressure. This experiment indicated than an allowed transition would have been detected at a concentration of 10^{10} molecules/cm^3 in the initial vibrational level.

1949

Bates, D. R., "The Earth's Upper Atmosphere", Mon. Not. Roy. Astron. Soc., 109, 215, (1949).

In this extensive paper on "Reports on the Progress of Astronomy", the topic of atomic nitrogen in the upper atmosphere is briefly discussed. The author states that unlike oxygen, nitrogen is extremely difficult to dissociate and that until a few years ago most investigators considered nitrogen would remain in the molecular state up to very great heights. The evidence for this was based on the presence of very intense bands of molecular nitrogen in the spectra of all aurora irrespective of their altitude.

Recently certain evidence indicates that atomic nitrogen is far from rate and may occur at comparatively low levels. One estimate gave a value of 4 x $10^{11}/cm^3$ for the number of N I atoms at 100 km altitude. The following process might explain the radiation

$$2N + X \longrightarrow N_2 + X'$$

$$X' \longrightarrow X + h\nu$$

in which X is some third body receiving excess energy from atomic nitrogen to emit the radiation.

While it is still a matter of controversy how much energy this mechanism might yield, a value of 7.38 ev has been suggested by some workers. Reference is made to the discovery of radiation near λ10,400 A by R. Herman, L. Herman, and J. Gauzit (1942) who found this radiation perhaps a hundred times more intense than the λ5577 line in the visible. Stebbins, Whitford, and Swings (1945) have shown that if 7.38 ev is the energy available, only the zeroth vibrational level would be excited since the next vibrational level requires 7.5 ev.

Bates, D. R., "The Intensity Distribution in the Nitrogen Band Systems emitted from the Earth's Upper Atmosphere", Proc. Roy. Soc. (London), A 196, 217, (1949).

This is an extensive theoretical discussion of the intensity distributions in the negative, first positive, and second positive bands of nitrogen. The results are compared with the intensity distributions observed from upper atmospheric sources. The author states that such information is useful in establishing the validity of proposed identifications, and in determining the mechanisms that are responsible for the excitation.

With reference to atomic nitrogen the author states that it is improbable that the radiation at about λ3471 A reported by Götz (1941) is

due to the (3, 4) band λ3469 A of nitrogen. The correct identification is doubtless the forbidden doublet of atomic nitrogen $^2P \rightarrow {}^4S$, λ3466 A, whose presence was first observed by Slipher and Sommer (1929) in studies of low latitude aurorae. The infrared emission radiation near λ10, 440 A observed in the night sky spectrum is also discussed. Reference is made to Herman, Herman, and Gauzit (1942) who discovered this radiation. The radiation at λ10, 440 A is extremely strong in comparison with any other in the night sky spectrum, even much more intense than the λ5577 A, the forbidden green line of O I.

Considering the process

$$N\,(^4S) + N\,(^4S) + N_2\,(X\ ^1\Sigma_g^+) \rightarrow N_2\,(B\ ^3\Sigma_g) + N_2\,(X\ ^1\Sigma_g^+) \qquad (a)$$

suggested by Stebbing, Whitford, and Swings (1945), and the process

$$N\,(^4S) + N\,(^4S) + X \rightarrow N_2\,(A\ ^3\Sigma_g^+) + X \qquad (b)$$

and if the thickness of the luminous layer is taken as 10 km, then the rate of process (a) is $8 \times 10^4/cm^3/sec$ and that of process (b) must be $8 \times 10^5/cm^3/sec$. From these data the author states that about 8×10^{10} nitrogen atoms/cm^3 would be lost during the aurora of a night. Since Stebbing, Whitford, and Swings found that the infrared emission was maintained throughout the hours of darkness, this would indicate that only a small fraction of the free nitrogen atoms disappear in a night. Thus the peak concentration of nitrogen atoms must be about $4 \times 10^{11}/cm^3$.

Bates, D. R., "The Emission of the Negative System of Nitrogen from the Upper Atmosphere and the Significance of the Twilight Flash in Theory of the Ionosphere", Proc. Roy. Soc. (London), A 196, 562, (1949).

This is a thorough study of the cause of the emission of the negative

band system of nitrogen from the upper atmosphere during twilight. The following two possible excitation mechanisms were studied.

$$N_2\ (X\ ^1\Sigma_g^+) + h\nu \longrightarrow N_2^+\ (B\ ^2\Sigma_u^+) + e^- \qquad \text{(a)}$$

$$N_2^+\ (X\ ^2\Sigma_g^+) + h\nu \longrightarrow N_2\ (B\ ^2\Sigma_u^+) \qquad \text{(b)}$$

With reference to atomic nitrogen in the upper atmosphere the author states that there is spectroscopic evidence that on at least some occasions nitrogen is partly in the atomic form. Reference is made to Dufay (1934); Stebbing, Whitford, and Swings (1945); Götz (1947); Bernard (1947); and Bates (1948, 1949). It is stated that the degree of dissociation and the region of dissociation are unknown. As a result the possibility cannot be ignored that at the altitudes considered in the paper molecular nitrogen is rare. However auroral spectra show that there is some molecular nitrogen even at 1000 km, but its fractional concentration cannot be estimated reliably.

The possible influence of atomic nitrogen is considered. Table 8 in the paper compares, for various degrees of dissociation, the electron production rates in the F_2 layer due to atomic oxygen and atomic nitrogen; the total particle concentration is also given. Neither diffusive separation of the atmospheric constituents nor the small interaction of one absorption process on the other were considered. From the compilation it was concluded that the ions formed in the F_2 layer are atomic and not molecular. This is important in any study of the recombination processes operative.

Cario, Gunther and Ludolf H. Reinecke, "Die Dissoziationsenergie des Stickstoff Moleculs und ihre Bedentung fur das Nachleuchten des Aktiven Stickstoffs", Abhandlungen der Braunschweigischen Wissenschaftlichen Gesellschaft, 1, 8-13, (1949).

This article reports the dissociation energies of the nitrogen molecule according to Herzberg (7.38 ev), Gaydon (9.76), and Schmid and

Gero (5.0 ev). Morse potential curves are included. Extrapolation of the experimental curve of Morse with the aid of Hulburt and Hirschfelder functions leads to a value of 9.76 ev for $D(N)_2$. The authors applied this value which led to the conclusion that the recombination of two normal 4_S nitrogen atoms is responsible for delivering the energy of the afterglow of active nitrogen. A bibliography of 15 references pertinent to the topic of active and atomic nitrogen is included.

Dufay, Jean, "Permitted Lines of Neutral Atoms of Oxygen and Nitrogen of the Aurora", Compt. rend., 228, 496, (1949).

The author states that the identification of spectral lines due to O I and N I is new evidence for the dissociation of molecular nitrogen molecules in the upper atmosphere.

Elvey, C. T. and Don Williams, "Recent Spectroscopic Investigations of the Aurora, Night Sky, and Twilight", Astron. J., 54, 184, (1949).

This is a brief preliminary report on the observations of the aurora, night sky, and twilight. The purpose of the study was to investigate the physics of the upper atmosphere. The observations were made at College, Alaska and at China Lake, California near the Naval Ordnance Test Station, and were sponsored by the Office of Naval Research.

The preliminary study indicated that spectra of the tips of auroral rays show an enhancement of several sharp lines which the authors interpret as probably atomic oxygen and nitrogen, and also wide symmetrical lines at wavelengths coincident with H_β and H_γ.

Greenblatt, J. H. and C. A. Winkler, "The Reaction of Nitrogen Atoms with Ethylene", Can. J. Research, 27B, 721-731, (1949).

The authors state in the introduction that few kinetic data for the reactions of nitrogen atoms are recorded, due to the uncertainty of

whether atoms or metastable molecules are the reactive species after nitrogen has been subjected to a condensed or electrodelss discharge. In the present research the reaction of atomic nitrogen with ethylene was studied by the Wood-Bonhoeffer method. The experimental procedure is described in detail.

The data are recorded in Tables I, II, and III of the paper. The products formed were hydrogen cyanide, ethane, and a polymerizable material. It was found that the yield of hydrogen cyanide accounted for 70% of the ethylene consumed. A mechanism is presented for the reaction which involves the rupture of the ethylene double bond with the formation of hydrogen cyanide and a methyl radical, the latter reacting further with nitrogen atoms.

$$C_2H_4 + N \rightarrow \text{Activated Complex} \rightarrow HCN + CH_3$$

$$CH_3 + N \rightarrow HCN + 2H$$

The activation energy of 6.9 kcal was calculated from collision yields using the relation

$$\text{Collision yield} = Ae^{-E/RT}.$$

The steric factor, A, was assumed to have a value of 0.1.

Pavlova, E. N., "Infrared Emission of the Night Sky", Doklady Akad. Nauk. S. S. S. R., 65, 831, (1949).

The band at 10,440 A is most intense in the spectral interval $\lambda\lambda$ 11,000 - 8000 A. The λ10,440 A band is ascribed to recombination of nitrogen atoms by the action of ultraviolet radiation from the sun according to the following mechanism.

$$N + N + N_2 \rightarrow N_2 + N_2^* \; (B\ ^3\Pi)$$

1950

Barbier, D. and D. R. Williams, "Observations of the Aurora Borealis", J. Geophys. Research, 55, 401, (1950).

The work reported in this paper was a part of the project on physics of the upper atmosphere, for which the Aerophysics Branch of the U. S. Naval Ordnance Test Station had organized a mission for making spectrographic and photoelectric-photometric observations of the aurora borealis in Alaska. The studies reported here were made during the period 26 January to 25 February 1949 at Field Station No. 1 of the Geophysical Observatory, University of Alaska, College, Alaska.

Figure 1 in the paper gives a reproduction of the more intense half of six auroral spectra. The N I line $\lambda 3466$ A is shown in the spectra and is clearly visible when ever the exposure time for the spectrum was sufficient. This evidence confirms the presence of the heretofore debatable line, N I 3467 A, in the auroral spectrum.

Bates, D. R., "Dissociative Recombination", Phys. Rev., 78, 492, (1950).

In this letter to the editor Bates considers the process of dissociative recombination of molecular ions in the study of decay of ionization.

$$XY^{+} + e^{-} \longrightarrow X' + Y'$$

This reaction was treated as taking place in two stages. The following formula was derived for the recombination, α.

$$\alpha(\epsilon) = \left\{ rh^3 f(\epsilon) / 8\pi \quad (2m^3 \epsilon)^{1/2} \quad [\, t_A(\epsilon) + t_S(\epsilon)] \right\}$$

where r is the ratio of the statistical weight of XY' to that of XY^{+}, h is Planck's constant, and m is the electronic mass. As usual $f(\epsilon)$ is such that $\int_{\epsilon} f(\epsilon)\, d\epsilon$ is unity.

The symbol $f(\epsilon)$ is the familiar Franck-Condon factor measuring the degree of overlap between the nuclear wave functions concerned in the initial transition, $t_A(\epsilon)$ is the time associated with the auto-ionization process, and $t_S(\epsilon)$ is the time for effective separation to occur. The derived expression gives the rate at which electrons of energy, ϵ, enter the excited state.

Bates, D. R. and M. J. Seaton, "Theoretical Considerations Regarding the Formation of the Ionized Layers", Proc. Phys. Soc. (London), 63 B, 129, (1950).

This is a theoretical discussion of the detailed mechanisms involved in the formation of the E, F_1, F_2, and D layers by solar ultraviolet radiation. In regard to atomic nitrogen the authors state that the atmosphere above about 100 km altitude is generally considered to be composed mainly of atomic oxygen and molecular (or perhaps atomic) nitrogen. The possibility that the ionization of atomic nitrogen

$$N + h\nu \longrightarrow N^+ + e^-$$

may contribute to the formation of both the F_1 and F_2 layers is not excluded.

The following values are given for the ionization potential and absorption cross—section of atomic oxygen and nitrogen.

	Ionization potential ev	Absorption cross section at spectral head (A) (10^{-18} cm^2)
Atomic oxygen (0)	13.5	2.6
Atomic nitrogen (N)	14.5	9

The standard Chapman formula $n(X) = \cos X/HA$

is employed to calculate the concentration, where n(X) is the concentration of the atoms or molecules X responsible for the ionization, X is the solar zenith angle, H is the local scale height, and A the relevant absorption cross section. Cos X is adopted as having the value 0.8. Taking H to be 30 km, the value of n(N) required in the Chapman-like F_1 layer was calculated to be $3 \times 10^{10}/cm^3$, compared with a total particle concentration of $1 \times 10^{11}/cm^3$. It was considered that this high degree of dissociation was not impossible.

$$n(\dot{N}) = 0.8/3 \times 10^6 \times 9 \times 10^{-18}\ cm^3 = 3 \times 10^{10}/cm^3$$

Cario, G. and L. Reinecke, "Energy of Dissociation of Nitrogen Molecules and Luminosity of Active Nitrogen", Angew. Chem., 62, 48, (1950).

Reference is made to the values of 7.38 ev by Herzberg, 9.76 ev by Gaydon, and 5.0 ev by Schmid and Gero for the energy of dissociation of nitrogen molecules, $D(N_2)$. The potential curve of the $X\ ^1\Sigma_g$ ground state of N_2 was determined up to a vibration energy of 6.5 ev after the Rydberg method. By extrapolation of the Morse curve, the authors calculated the value 9.76 ev for $D(N_2)$, which supports that of Gaydon. The value 9.76 ev of the recombination of two normal ^4S nitrogen atoms was considered sufficient to provide the energy of the afterglow of active nitrogen. It is in agreement with the relation between intensity of the afterglow and temperature (250°K), explaining a recombination mechanism which leads over the predissociation limit to the $B\ ^3\Pi_g$ state.

Courtes, Georges, "The Ray (^4S - ^2D) of Atomic Nitrogen observed at Twilight", Compt. rend., 231, 62, (1950).

The author reports that the sharp line λ5199.6 A was identified as the

forbidden transition $^4S \rightarrow {^2D}$ of N I in the spectrum of twilight. Hitherto this radiation had only been observed in the auroral light.

Divari, N. B., "The Pressure exerted by Solar Radiation on the Atoms of Certain Gases", Astron. Zhur., 27, 351, (1950).

The English abstract of this paper is contained in Astronomical News Letter, (Harvard), No. 55, (15 February 1951). The following equation is given.

$$1 + \mu = \left\{ [(2 \pi^2 h \epsilon^2 f)/(M m_H m c \lambda^3 g_s)].r. [1/e^{(hc)}/(\lambda kT) - 1)] \right\}$$

$1 + \mu$ is the ratio of the acceleration due to radiation to that due to gravity, ϵ and m are the charge and mass, respectively, of the electron, m_H is the mass of the H atom, M is the mass of the given atom, λ is the wavelength of the radiation absorbed, g_s is the gravitational acceleration at the sun's surface, f is the oscillator strength, r is a correction factor (having the value 0.1 in most cases); the remaining symbols have their usual physical meaning.

The value of $1 + \mu$ for the H_α line is 238, which was considered insufficient to permit escape of hydrogen from the earth's atmosphere. The value of $1 + \mu$ for atoms in the ground state are much lower. The escape from the earth's gravitational field of nitrogen and oxygen atoms was also considered impossible because of solar radiation pressure alone.

Fesenkav, V. G. (Mountain Astrophys. Observatory, Akad. Sci, Kazakh, S. S. S. R. "A Gaseous Tail of the Earth", Izvest Akad, Nauk S. S. S. R., Ser. Fiz., 14, 257, (1950).

This paper describes the outermost atmosphere of the earth as forming a tail which consists of dissociated oxygen, nitrogen, and hydrogen. The atmosphere is in the form of a conoid envelope re-

sembling the tails of comets of Type I.

Gartlein, C. W., "Aurora Spectra showing Broad Hydrogen Lines", Trans. Am. Geophys. Union, 31, 18, (1950).

This is a brief report of the study of aurora at Cornell University. A brief description is given of the spectrograph used. The following usual well known features of auroral spectra appear regularly. (a) The second green line of oxygen is reported to be resolved into the bands at λλ5296 and 5250 A; (b) the negative nitrogen bands at λλ5228 and 5145 A; and (c) the sharp forbidden N I lines at 5199 A. A brief examination of the H_β, 4861 A, and H_γ, 4340 A, and the broadening of these lines included in the discussion.

Jose, P. D., "The Infrared Spectrum of Lightning", J. Geophys. Research, 55, 39, (1950).

The following papers are listed in the references at the end of the present paper as evidence of the importance to atmospheric physics of the spectroscopy of lightning: (a) H. Israel and K. Wurm, Naturwiss. 29, 778, (1941); (b) M. Nicolet, Ciel et Terre, 59, No. 3, (1943); (c) J. Dufay, Cahiers phys., No. 14, 64, (1943); (d) M. Dufay, Compt. rend., 225, 1079, (1947); and (e) J. Dufay and Tcheng Mao-Lin, Compt. rend., 228, 330, (1949).

The investigations reported in these papers have covered the spectral region λλ 2910 to 6570 A. The following atomic lines have been identified in this region in the spectrum of lightning: H, N I, N II, O I, and O II.

The author states that the purpose of the present work was to extend the spectral range of the spectrum of lightning toward the infrared. The instrument employed was the B-spectrograph, consisting of an F/4 aluminum-on-glass parabolic collimator, a plane aluminim-

on-glass grating, and an F/0.65 solid Schmidt Camera. The spectral range extended up to λ8800 A in the infrared. In the range λλ 7400 to 8800 A the radiations were found to be due exclusively to O I and N I. Table 1 in the paper gives the lines measured and the identifications. Figure 1 shows an enlargement of two of the spectrograms together with a comparison spectrum of the neon glow-lamp.

Kaplan, Joseph, "Laboratory Studies Related to the Physics of the Upper Atmosphere", I.U.G.G. Assoc. Terrest. Mag. Elect., I.A.T.M.E. Bull., No. 13, pp. 474-479, (1950).

This is a report given at the Oslo Meeting, 19-28 August 1948, of the International Association of Terrestrial Magnetism and Electricity of the I.U.G.G. The author has reported in brief form some of the results of experiments in his own laboratory. The results were achieved by the discovery and study of two distinctive afterglows in nitrogen and one in oxygen. The two nitrogen afterglows are distinguished from the Lewis-Rayleigh afterglow and are referred to as the strong and weak auroral afterglows of nitrogen.

These afterglows are fully described. Reference is made to the observations of Whitford and Swings [Astron. J., 101, 155, (1945)], who ascribed the emission of the (0,0) band to the conversion of the energy of dissociation $D(N_2)$ into excitation in the three-body collision

$$N + N + N_2 \longrightarrow N_2 + N_2^{exc.} \qquad \text{(a)}$$

Another possible origin of the (0, 0) band is the following reaction

$$N_2\ [A\ ^3\Sigma(v=o)] + N\ ^2P \longrightarrow N_2\ [B\ ^3\Pi(v=o)] + N\ ^2D \qquad \text{(b)}$$

$$6.14\ \text{ev} + 3.56\ \text{ev} \longrightarrow 7.31\ \text{ev} + 2.37\ \text{ev}$$

The author tentatively concludes that neither reaction (a) nor (b) occurs as often as the following

$$N' + N'' + M \longrightarrow N_2\ [B\ ^3\Pi\,(v=o)] + M' \qquad (c)$$

where N' and N'' represent nitrogen atoms in one of the two low-lying metastable states and M is a third body, N_2 or O_2. The dissociative recombination mechanism

$$N_2^+ + e^- \longrightarrow N' + N'$$

is also briefly discussed. It is proposed that both in the upper atmosphere and in the auroral afterglow low velocity electrons remove both atoms and molecules from metastable states and that subsequent collisions excite allowed radiations such as the first negative bands.

Kaplan, Joseph, "Heat of Dissociation of Nitrogen", Phys. Rev., 78, 93, (1950).

This is an abstract of a paper read at the 296th regular meeting of the American Physical Society at Stanford University, 29-30 December 1949. The author has presented a new method for selecting between the Herzberg value of 7.384 ev for the heat of dissociation, $D(N_2)$, of N_2 molecules ($X\ ^1\Sigma$) into two normal nitrogen atoms (^4S) and between Gaydon's value of 9.764 ev. The author states that it is based on experimental proof that the $A\ ^3\Sigma$ level of N_2 dissociates into one normal and one excited atom. If the value of $D(N_2)$ were 9.764 ev it would have to dissociate into two normal atoms.

The experimental proof cited is the result of observations which show that those Begard-Kaplan bands which originate on $v' = 0$ are observed in auroral afterglows only when metastable atoms in either the ^2P or ^2D levels are involved. Assuming that the products of dissociation of the $A\ ^3\Sigma$ level are ^2P and ^4S, and D = 7.38 ev, the Birge-Sponer

extrapolation for this level is too small by 0.08 ev. If the dissociation products were in the ^2D and ^4S levels, the extrapolation is too great by 1.10 ev. The author considers this to be a reasonable excess and favors the Herzberg value of 7.384 ev.

Meinel, A. B., "Strong permitted O I and N I Lines in the Infrared Auroral Spectrum", Trans. Am. Geophys. Union, 31, 21, (1950).

With reference to atomic nitrogen the author states that certain auroral radiation can be attributed to N I. The strong features at 8684 and 8712 A which are superimposed on the (2, 1) transition of the first positive system of N_2 coincide with the strongest lines of the $3p\ ^4D^0 \longrightarrow 3s\ ^4P$ transition of N I. The author states that three other N I transitions appear to be present, but they are considerably weaker. An energy level diagram for both O I and N I is included.

Petrie, W., "The Near-Infrared Spectrum of the Polar Aurora", J. Geophys. Research, 55, 143, (1950).

The grating spectrograph used at the University of Saskatchewan during auroral displays is described. The wavelengths of the auroral radiations were determined by measuring their positions from a neon comparison-spectrum superimposed on each plate. The method for obtaining intensities is described. The comparison of the intensities of the O I and N I lines was obtained from the following relation.

$$I = N\ A\ h\nu = \frac{64\ \pi^4\ \nu^4}{3c^3}\ \frac{N}{\omega_m}\ \frac{e^2 a^2}{4 1^2 - 1}\ s\rho\ \ldots\ldots$$

in which N is the number of atoms in the upper level involved in the production of the spectral line,

A = the Einstein transition probability coefficient,

ν = frequency of the emitted radiation,

ω_m = the statistical weight of the upper level,

a = the radius of the first Bohr orbit,

1 = the larger of the initial or final values of the orbital quantum-number of the "jumping electron" associated with the two electron-configurations from which the transition arises,

s = the theoretical line "strength",

ρ = the radial quantum-integral

$$R_{nl} R_{n'l'} r^3 dr .$$

where R_{nl} and $R_{n'l'}$ are the radial wave-functions associated with the two electron-configuration; h, c, and e have their usual meanings. The ratio of the numbers of nitrogen and oxygen was found to be 1.6. From infrared spectra of the aurora it was deduced that N I and O I atoms are not excited to any energy levels with energies exceeding 12 ev. From a comparison of the intensities of N I and O I lines it was deduced that a considerable fraction of the N_2 molecules are dissociated at 60 miles. A temperature of $7000^{\circ}K$ for the excitation temperature was indicated from the intensities of the O I lines.

Petrie, W., "The Near Infrared Spectrum of the Polar Aurora", Phys. Rev., 77, 720, (1950).

The author reports that during 1948 the infrared spectra of the aurora had been obtained by Meinel (1948) at the Lick Observatory and by the author himself at the University of Saskatchewan. Features of the spectra include low energy level permitted multiplets of O I and N I. It appeared that aoms of oxygen and nitrogen are not excited to levels with energies greater than about 11.5 ev. From the relative intensities of the N I and O I lines it was deduced that the ratio of the numbers of nitrogen and oxygen atoms in low energy levels is of the order of 1.5.

Robley, R., J. Bricard, and A. Kastler, "The Spectrum of the Aurora Borealis of 25-26 January 1949", Ann. geophys., 6, 66, (1950).

The following lines and bands in the spectrum of the aurora borealis were observed and identified as O I, O II, O III, N I, N II, Na, N_2, and N_2^+. It is stated that the radiation at λ 5205 A is strong, and that this is additional evidence for the presence of the forbidden transition $^4S \rightarrow {}^2D$ of N I in the upper atmosphere confirming the results of Slipher and Sommer, Götz and Dufay.

Rodinov, S. F., "Emission and Absorption of Light in Some Atmospheric Layers", Izvest. Akad. Nauk S.S.S.R., Ser. Fiz., 14, 247-256, (1950).

The author reports that the infrared radiation of the night sky was studied at an altitude of 2200 and 4200 meters. A photomultiplier tube with a sensitivity 10^{-13} lm and a filter passing only wavelengths between 900 and 1100 mμ were used. The height of the emitting layer was calculated to be 900 km. The radiation was assumed to be emitted by nitrogen molecules.

Ufford, C. W. and R. M. Gilmour, "Multiplet Intensities for the Lines ^4S - ^2D of N I", Astrophys.J., 111, 580, (1950).

It had been suggested to the aurthors that the forbidden lines of N I might appear in the spectrum of the night sky. Reference is made to Bowen and Wyse [Lick Obs. Bull., 19, 1, (1939); Astrophys. J., 95, 358, (1942)] who observed the lines λλ5198.5 and 5200.7 A of N I, corresponding to the $^4S_{3/2} \rightarrow {}^2D_{3/2}$ and $^4S_{3/2} \rightarrow {}^2D_{5/2}$ transitions in the ground p^3 configuration, in the spectrum of planetary nebulae.

The authors in the present paper have calculated the relative strengths of the transitions $1s^2 2s^2 2p^3\ {}^4S_{3/2} \rightarrow {}^2D_{5/2}$ and $1s^2 2s^2 2p^3\ {}^4S_{3/2} \rightarrow {}^2D_{3/2}$ in N I, including spin-spin interaction. The theoretical value of the ratio of the intensities of the two components of the ${}^4S \rightarrow {}^2D$ multiplet was found to be

$$r = \frac{I({}^4S_{3/2} \rightarrow {}^2D_{5/2})}{I({}^4S_{3/2} \rightarrow {}^2D_{3/2})} = 0.83$$

Vegard, L., "Properties of the Upper Atmosphere Revealed Through Spectral Analyses of Aurorae and Twilight", I.U.G.G. Assoc. Terrest. Mag. Elect., I.A.T.M.E. Bull., No. 13, pp. 479-490, (1950).

This is a paper read at the Oslo meeting, August 19-28 (1948). The author considers molecular nitrogen to be a predominant component all through the auroral region. With reference to atomic nitrogen in the upper atmosphere, if it is dissociated to any marked degree lines from atomic nitrogen could be expected in the spectrum of auroral luminescence. The transitions between metastable N I states of the neutral atom should give a green doublet (5197.7, 5200.8) with an average of 5199.3 A and a line 3466.5 A. The author observed on a considerable number of auroral spectrograms a sharp line with a wavelength 5203 A. Since this differs from the mean wavelength of the doublet by 4 A the difference was considered too great to be accounted for by errors. The moderately strong line 3467.5 in the ultraviolet was also observed. The difference of 1 A unit between the wavelength of this line and the forbidden N I line was considered greater than a possible error. It was concluded that the forbidden N I line 3466.5 A does not appear in the auroral spectrum.

Vegard, L., "New Investigation of the Spectrum of the Aurora Borealis", Compt. rend., 230, 1884, (1950).

This is a report of Vegard's observations of the visible region of the spectrum of the aurora borealis. The presence of approximately 115 lines and bands was observed in the spectrum of the aurora taken on the night of 23-24 February 1950. The presence of N I and N II lines was definitely established.

Vegard, Lars, "Important New Results in the Study of the Aurora Borealis and the Physics of the Ionosphere", Ann. geophys., 6, 157, (1950).

This is an anlysis of a spectrogram of the auroral spectrum on 23-24 February (1950) at Oslo. The spectrogram in the region $\lambda\lambda$3900 - 6300 A showed 140 vibrational bands and atomic lines, of which 54 had not been previously observed. A large number of the lines were identified as due to atomic nitrogen and oxygen in both the neutral and ionized state. The N I doublet $\lambda\lambda$ 5197.7 - 5200.8 A resulting from the forbidden transition $^4S_{3/2} \rightarrow {}^2D_{3/2, 5/2}$ was very distinct.

Vegard, Lars and Hans Raastad, "The Intensity Distribution within the Nitrogen Spectrum from Canal Rays and Negative Glow, with reference to the Auroral Luminescence", Geofys. Publ., Oslo, 17, No. 7, (1950).

The authors state that the fact that nitrogen bands and particularly those of the negative group appear with great intensity in auroral luminescence even at the upper limit of the longest auroral streamers is of great importance and value for the study of the physics of the upper atmosphere.

The experimental procedure is described in detail. The discussion

includes (a) the spectra from canal rays and the negative glow, (b) the atomic lines in the canal ray spectrum, (c) the variations of intensity distribution of the negative bands by change of the energy of the exciting electric rays, (d) intensity distribution within the negative group in nitrogen-helium mixtures, and (e) a comparison with results found by other investigations.

In summarizing the authors conclude that the peculiar intensity distirubtion sometimes found from the auroral spectra at high altitudes is explained by means of the observed canal ray effect. It is also suggested that a number of N II lines appearing in the canal ray spectrum are probably present in the auroral luminescence.

Weissler, G. L. and E. I, Mohr, "Absolute Absorption Coefficients in N_2 in the Vacuum Ultraviolet", Phys. Rev., 77, 741, (1950).

This is an abstract of a paper read at the 295th meeting of the American Physical Society held in Chicago, 25-26 November 1949. The authors state that absolute absorption coefficients k_λ in N_2 for light in the wavelength region $\lambda\lambda$600 to 1300 A were measured. A grazing incidence two-meter vacuum spectrograph was used, and a Lyman source provided the wavelength continuum. Details of obtaining the exposures are described.

1951

Branscomb, Lewis M., "The Infrared Spectrum of Active Nitrogen", Phys. Rev., 82, 83-86, (1951).

The primary reaction leading to the Lewis-Rayleigh afterglow of active nitrogen is considered to be the recombination of two nitrogen atoms in the presence of a third body. If the dissociation energy of nitrogen is 7.383 ev, the above reaction would give rise to a molecule in either the metastable $A\ ^3\Sigma$ level or in the $v = 0$ level of $B\ ^3\Pi$.

Mention is made of the controversial value of the dissociation energy of molecular nitrogen. Reference is made to Gaydon's value of 9.765 ev. The analogy between the Lewis-Rayleigh afterglow of active nitrogen and the air glow of the earth's atmosphere is discussed. The excitation process for the 10,440 A band is described.

Chapman, Sydney, "Some Phenomena of the Upper Atmosphere", Proc. Phys. Soc. (London), 64 B, 833, (1951).

This paper is Professor Chapman's presidential address delivered 2 May 1951 before the Physical Society of London. Brief mention is made about the uncertainty regarding the composition of the atmosphere at high levels due to lack of data on the proportion of atomic nitrogen present.

The equation of static equilibrium, $dp = -\rho\, g dh$, relates the decrement of pressure dp with the increment of height dh, and with the density ρ and gravitational acceleration g. Since

$$p = knT$$

where k is the Boltzman's constant, n the number density (number of molecules per unit volume), and $\rho = n\overline{m}$, where $\overline{m}$ is the mean molecular mass, the following equation is obtained.

$$dp/p = -\overline{m}g/kT \ dh = -dh/H$$

if $H = kT/\overline{m}g = RT/\overline{M}g$ where R is the gas constant and $\overline{M}$ is the mean (chemical) molecular weight. The symbol H is called the "scale height". If H were constant, the variation of pressure with height is obtained from the equation

$p/p_o = e^{-h/H}$, where p_o is the value of p at zero

height. Actually H is not constant because T, g, and $\overline{m}$ (in certain ranges of height) vary with height. Because $\overline{M}$ is a variable above the homopause, knowledge of the dissociation of both molecular nitrogen and oxygen would be most valuable information to evaluate the influence of the change in $\overline{M}$ upon H and hence temperature with height.

Douglas, A. E. and G. Herzberg, "Predissociation and Dissociation of the N_2 Molecule", Can. J. Phys., 29, 294-300, (1951).

The authors have investigated the predissociation in the upper state of the Lyman-Birge-Hopfield bands of nitrogen. It was found that there was a breaking off of the fine structure above $\nu^1 = 6$, $J^1 = 13$, both in the P and Q branches. The authors' observations in this study appeared to definitely eliminate the value 8.565 ev for the dissociation energy of the molecule.

The two values 7.373 ev and 9.756 ev for $D(N_2)$ still remain at this time (1951) possible alternatives. The acceptance of the higher value (9.756) would involve the assumption that the predissociation in the a $^1\Pi_g$ state results from normal atoms and that this $^5\Sigma_g^+$ state is not purely repulsive.

Dufay, Maurice, "The Forbidden Line $^4S - ^2D$ of the Neutral Nitrogen Atom in the Spectrum of the Night Sky and at Twilight", Compt. rend., 233, 419, (1951).

In this paper Dufay has studied the results of observations of the night sky and twilight during June 1950 to July 1951. He found the appearance of the line $^4S \rightarrow ^2D$ of N I on 25 of the spectrograms. The line appeared during summer months to have greater intensity in the sky at twilight than after twilight. This phenomenon was not observed during winter months. From an average of 18 measurements the wavelength was determined to be 5199.1 A.

The author states that only a slight degree of dissociation is sufficient for observing the intensity of the line, and that atoms of neutral atomic nitrogen in the ^4S state may be raised to the ^2P state by absorption of ultraviolet radiation $\lambda 3466$ A. In returning to the ground state, the mechanism proceeds through successive emission of the forbidden lines $\lambda\lambda 10,406$ and 5199 A.

Lukashenya, V. T. and V. I. Krasovaskii, "Details of the Night-Sky Spectra from 9500 to 12,000 A", Doklady Akad. Nauk S.S.S.R., 79, 241. (1951).

The observations on the night sky spectra were obtained by means of two grating spectrographs with dispersions of 850 and 150 A/mm. The resolving power was 30 and 5 λ. The spectra showed a large number of lines not previously reported by the authors. Among others the line of the transition of the doublet states ($^2P \rightarrow {}^2D$) of atomic nitrogen was identified.

Meinel, A. B., "The Auroral Spectrum from 6200 to 8900 A", Astrophys. J., 113, 583, (1951).

This is a report of the exposures of varying duration within the spectral range from 6200 to 8900 A during an intense auroral storm 18 and 19 August 1950. With reference to N I emissions the author states that the evidence to date had been based on the strong emission near 8680 A from the 3s $^4P \rightarrow$ 3s $^4D^0$ transition of N I. The identification of this complex group of emissions is difficult, and the 3s $^4P \rightarrow$ 3p $^4P^0$ transition of N I would be a better test. The latter occurs in a region free from the other auroral lines near 8216 A.

Reference is made to Dufay (1949) who discovered the 3s $^4P \rightarrow$ 3p $^4P^0$ transition and suggested that it might account for the weak emission in this region previously reported by Meinel (1948). The

author states that the spectra observed and discussed in the present paper shows conclusively that the 3s $^4P \rightarrow$ 3p $^4P^o$ transition of N I is present in the aurora. The 3s $^4p \rightarrow$ 3p $^4S^0$ transition of N I at 7468, 7442, and 7423 A was not observed. The evidence of the 8212 A N I emission was considered as sufficient evidence to establish the presence of atomic nitrogen at low elevations during an aurora.

Meinel, A. B., "The Analysis of Auroral Emission Bands from the A $^2\Pi$ State of N_2^+", Astrophys. J., 114, 431-437, (1951).

The author states that the existence of an A $^2\Pi$ state of N_2^+ had been known for some time but that it had never been observed in the laboratory. Vibrational analysis of some unidentified auroral lines gave evidence that these auroral bands were due to transitions originating from the A $^2\Pi$ level of N_2^+ . A detailed analysis of these auroral bands is given in the present paper.

Mitra, S. K., "Atomic Nitrogen in Auroras", Nature, 167, 897, (1951).

The author states at the beginning of this paper that the presence of atomic nitrogen in auroras has been proved beyond doubt by the identification of the forbidden lines λ3466 ($^2P \rightarrow {}^4S$) and $\lambda\lambda$5200 - 5198 ($^2D \rightarrow {}^4S$). As evidence for this work of Tcheng Mao-Lin and Dufay [Cahiers phys., 8, 51, (1942)] and Bernard [Gassiot Committe Report, (1947), Physical Society, London, (1948)] is cited.

The purpose of the present paper was to show that dissociative recombination of N_2^+ (X') ions can also cause dissociation of nitrogen molecules and excitation of the resulting nitrogen atoms to the required metastable states. The reaction is represented as follows,

$$N_2^+ (X') + e^- \longrightarrow N(^2P) + N(^2D)$$

for which the author states that there is almost exact resonance if the dissociation energy of molecular nitrogen is 9.76 ev, a value obtained by Gaydon (1944). The energy value supplied on the left-hand side of the above equation is 15.58 ev (first ionization potential), the N_2^+ (X') ion being in the lowest vibrational level (v'' = O). The energy required on the right-hand side is 15.69 ev, the total energy required for dissociating the nitrogen molecule (9.76 ev), for exciting one nitrogen atom to the ^2P state (3.56 ev), and for exciting the other atom to the ^2D state (2.37 ev).

The author also states that the first negative bands in the auroral spectrum show that the excited N_2^+ (A') ions from which the bands originate are left, after emission, both in the lowest vibrational level (v'' = O) of the ground-state N_2^+ (X') and also in the higher levels (v'' = 1, 2, etc.). It is pointed out that the lifetime of the N_2^+ (X') ions in these low vibrational levels is fairly long. Thus the dissociative recombination takes place with N_2^+ (X') ions which are in the vibrational levels v'' = 1, 2, etc. and with energy slightly in excess of that demanded by the above reaction, thus having a very high probability. The author gives the above mechanism as explanation of the atomic nitrogen lines in the auroral spectrum.

A second alternative process of neutralization of the N_2^+ involving O^- ions is also considered, but Mitra finds the latter process to be much less probable. Reference is also made to Kaplan (1948) who considered the reaction

$$N_2^+ + e^- \longrightarrow N\,(\text{excited}) + N\,(\text{excited})$$

as playing an important role in the auroral afterglow laboratory experiments. Kaplan used 7.38 ev (Herzberg's value) for the dissociation energy of molecular nitrogen and assumed that both nitrogen atoms are in the ^2P state.

Mitra, S. K., "Dissociative Recombination of N_2^+ ions and some Nitrogen and Afterglow Phenomena", Sci. and Culture, 16, 488, (1951).

The author refers to his note in [Nature, 167, 897, (1951)] in which it was shown that dissociation of N_2 molecules in the aurora can be effected by the following dissociative recombination process.

$$N_2 + (X') + e^- \rightarrow N(^2P) + N(^2D)$$

Reference is made to Tcheng Mao-Lin and Dufay (1942) and Bernard (1948) who proved indisputably the presence of the atomic nitrogen lines $\lambda 3466$ A ($^2P \rightarrow {}^4S$) and λ 5200 - 5198 A ($^2P \rightarrow {}^2D$) in the auroral spectra.

The author states that if the N_2^+ (X') ion is in the lowest vibrational level then the energy supplied by the left hand side is 15.88 ev (first ionization potential of N_2), and that this falls just short of the energy demanded on the right hand side, 15.69 ev, which is the sum of the dissociation energy of the N_2 molecule, 9.76 ev, [Gaydon (1944)] and the energies of the two metastable N-atoms, 3.56 ev and 2.37 ev.

$$3.56 \text{ ev} + 2.37 \text{ ev} + 9.76 \text{ ev} = 15.69 \text{ ev}.$$

The deficiency of 0.11 ev was considered to be made up if the N_2^+ (X') ion is in some vibrational level $v'' > O$, which would allow almost exact energy balance. The purpose of the author's present paper was to show that the fact that dissociative recombination of N_2^+ (X') ions takes place when, and only when, the ion is in some vibrational level $v'' > O$ in the lowest level would explain some of the nitrogen afterglow phenomena. Both the temperature effect and dark modification are considered and discussed.

Vegard, Lars and G. Kvifte, "An Auroral Spectrogram and the Results Derived from It", Geofys. Publ., Oslo, 18, No. 3, (1951).

This is an excellent study of the spectrogram of a brilliant aurora observed at Oslo during the night of 23-24 February 1950. A description is given of the new spectrograph which was used on this occasion. The new spectrograph had two prisms and compared with the best spectrographs previously used in Norway. The dispersion was about twice as large and the light power more than 5 times greater.

An extensive table is included which lists the wavelengths and interpretation of about 114 lines in the spectral region 6300 - 3800 A that could be directly measured from the original plate, more than 50 of which had been previously observed. In the spectral interval 8860-6364 A, 13 lines of N I had been previously identified; within the interval 6364-3114 A, 102 lines of N I originate from neutral atomic nitrogen.

The forbidden transitions $({}^4S_{3/2} \rightarrow {}^2D_{5/2,\ 3/2})$ would give a doublet (5202, 5197 A). The components could not be separated even with the new spectrograph. If the components were equally strong the doublet would give a somewhat broadened line with an apparent wavelength of 5199.5 A. Vegard and Kvifte observed a broad line of moderate intensity which appeared at 5199 A on the Oslo spectrogram. This was taken as proof that this forbidden green N I line appears in the auroral spectrum.

The doublet corresponding to the allowed transitions $3p\ {}^2S_{1/2} \rightarrow 5d\ {}^2P_{3/2,\ 1/2}$ gives components of wavelengths 5201.8 and 5197.1 A with the mean 5199.5 A. The fact that the observed auroral line 5199 A is moderately strong while the allowed lines are very weak greatly favors the assumption that the auroral line 5199 A originates from the forbidden transition .

Bates, D. R., "Some Reactions Occurring in the Earth's Upper Atmosphere", Ann. geophys., 8, 194, (1952).

This is an excellent and thorough discussion of the photochemistry of nitrogen in the upper atmosphere. The author gives several reasons why the photochemistry for nitrogen in the upper atmosphere is much more difficult than that for oxygen.

(a) N_2 does not have an observable continuum in the spectral region where the solar flux is sufficiently intense to produce much dissociation, as is the case for O_2. As a result the primary process operative is not obvious. Also it must be relatively slow with complications arising due to diffusion.

(b) In considering the allotropic forms of oxygen, the other atmospheric constituents are regarded as chemically inert. Such a procedure is unjustified with nitrogen.

Reference is made to Herzberg and Herzberg (1948) who pointed out the following mechanism to account for the primary process in N_2 dissociation. Predissociation occurs in some of the bands of the Lyman-Birge-Hopfield system.

$$\left\{\begin{array}{c} N_2\,(X\ {}^1\Sigma_g^+) + h\nu\ (\sim 9.8\text{ ev}) \longrightarrow N_2\,(a\ {}^1\Pi_g) \\ N_2\,(a\ {}^1\Pi_g) \longrightarrow 2N \end{array}\right\} \qquad \text{(a)}$$

The following secondary processes are suggested as important above the $O - O_2$ transition zone.

$$N + N + M \longrightarrow N_2 + M \qquad \text{(b)}$$

$$N + O + M \longrightarrow NO + M \qquad (c)$$

$$N + NO \longrightarrow N_2 + O \qquad (d)$$

$$NO\ (X\ ^2\Pi) + h\nu\ (\sim 6.5\ ev) \longrightarrow NO\ (A\ ^2\Sigma^+ \text{ or } C\ ^2\Sigma^+)$$

$$NO\ (A\ ^2\Sigma^+ \text{ or } C\ ^2\Sigma^+) \longrightarrow N + O \qquad (e)$$

The following table was compiled from calculations given in the paper. The altitudes are 125 and 105 km, respectively, and the temperature at both levels was taken to be 300°K.

Actual Atmosphere

Total particle concentration $n(M)/cm^3$	Concentration atomic nitrogen $n(N)/cm^3$	Nitric Oxide Concentration $n(NO)/cm^3$	Pure Nitrogen Atmosphere Concentration N I $n(N)/cm^3$
1×10^{12}	2×10^8	3×10^6	8×10^9
1×10^{13}	4×10^7	1×10^8	8×10^9

The following dissociative recombination may occur in the region of the F layers.

$$N_2^+ + e^- \longrightarrow 2N\ . \qquad (f)$$

The yield of nitrogen atoms is possibly large, perhaps $10^3/cm^3/sec$. If this is the case the author states that the values in the above table would have to be raised upwards.

The author also presents a survey of the observational evidence for the occurrence of atomic nitrogen in the upper atmosphere.

(a) Courtes (1950) found that $\lambda 5199$ A appeared in some airglow spectra which he took just after sunset.

(b) M. Dufay obtained confirmatory spectra and later calculated the rate of formation of the N (^2D) atoms involved by the action of solar radiation through the mechanisms.

$$N(^4S) + h\nu \longrightarrow N(^2D) \qquad (g)$$

$$\left\{\begin{array}{l} N(^4S) + h\nu \longrightarrow N(^2P) \\ N(^2P) \longrightarrow N(^2D) + h\nu \end{array}\right\} \qquad (h)$$

The value obtained by Dufay was 4.5×10^{-11}/illuminated N-atoms/sec.

(c) Reference is made to Ufford and Gilmour (1950) who found the mean radiative life of N (^2D) to be about 20 hours.

(d) Lines of N I and N II have been identified in auroral spectra by Meinel (1950) and Gartlein (1950).

Assuming that the excitation arises from

$$N + e^- \longrightarrow N' + e^- \qquad (i)$$

$$N + e^- \longrightarrow N^{+\prime} + 2e^- \qquad (j)$$

the author states that several workers have attempted to deduce the degree of dissociation from their intensities. Bates considers these as unacceptable since the actual situation is more complicated than supposed, and points out that the following processes are possible:

$$N_2 + e^- \longrightarrow N + N' + e^- \qquad (k)$$

$$N_2 + e^- \longrightarrow N + N^{+\prime} + 2e^- \qquad (l)$$

The theory of the formation of F layers may eventually yield information on the abundance of atomic nitrogen.

Benson, James M., "Measurements of the Physical Properties of Active Nitrogen", J. Applied Phys., 23, 757-763, (1952).

A brief summary is given in the introduction of the papers of theories and experiments by E. P. Lewis, Lord Rayleigh, S. K. Mitra, and Kaplan. Various physical properties of a stream of active nitrogen are described with the view that the measurements might provide new information for examining the theories of the nitrogen afterglow.

Measurements were made of the heat released during the decay of the afterglow, the viscosity of active nitrogen, the free electron density (electrical properties), corona discharges in the stream, microwave measurements, and the effect of a magnetic field on measurements in the stream. Flow-sheets are included for the arrangement and operation of the various experiments.

The heat released during the decay of the afterglow from calorimeter measurements indicated about 22.3 calories per gram of the gas which corresponded to an excitation of one part in 3.50 of the molecules present to an energy of 9.6 electron volts. Ionization in a stream of active nitrogen was shown to be incidental rather than essential to the production of the Lewis-Rayleigh afterglow. About one free electron for each 2.3×10^8 molecules in the stream was indicated from the microwave measurements of the free electron density in a stream of active nitrogen.

Cario, G. and U. Stille, "Excitation and Course of the Auroral Afterglow in Nitrogen", Z. Physik, 133, 209-228, (1952).

The authors state that the significant mechanisms for the intense excitation of the negative bands are collisions of the 2nd kind between nitrogen molecule ions and metastable nitrogen atoms in the ^2P state. The 2nd and also the 1st positive bands of N_2 are excited by two-body collisions

between metastable molecules, and also by recombination of nitrogen atoms by three-body collisions. The theory is discussed in detail. Many literature references are included of previous investigations on the topic of the nitrogen afterglow.

Clark, K. C., "Ionospheric Absorption by N_2 and O_2 of Certain Ultraviolet Solar Wavelengths", Phys. Rev., 87, 271, (1952).

In the introductory portion of this paper there is a general discussion of the ionization of the upper atmosphere by the absorption of solar radiation. Reference is made to the fact that atomic nitrogen is observed in auroras, but that there is no agreement on the degree of dissociation of molecular nitrogen.

The paper reports the author's measurements of the absorption coefficients of N_2 and O_2 of the emission from the H Lyman series 2-7, the resonance line 584 A of He I, and twenty lines of H_2 between 980 A and 850 A. Ionospheric layer heights have been calculated and are included in the paper. The laboratory measurements were carried out at the Lyman Laboratory of Harvard University.

Deb, S., "Nitrogen in the Upper Atmosphere", J. Atm. Terrest. Phys., 2, 309, (1952).

The author states in the introduction that the identification of the forbidden lines $\lambda 3466$ ($^2P \rightarrow {}^4S$) and $\lambda 5198$ ($^2D \rightarrow {}^4S$) in the auroral spectrum proves conclusively the presence of atomic nitrogen in the upper atmosphere, at least in the auroral regions. No dissociation process by direct absorption of solar ultraviolet radiation, as in the case of O_2, is known for N_2.

The purpose of the present paper was to investigate the probable distribution of atomic nitrogen in the upper atmosphere by considering two

processes: that according to Herzberg and Herzberg (1948) in which there may be predissociation of N_2 molecules by absorption in the Lyman-Birge-Hopfield band within the range 1150-1250 A, and, according to Mitra (1951), by dissociative recombination of N_2^+ ion and electron to produce excited nitrogen atoms.

The Herzberg and Herzberg process considers N_2 molecules to be excited to v' = 6 - 9 of the (a $^1\Pi_g$) state by absorption in the range 1150-1250 A and to dissociate by radiationless transition.

$$N_2 + h\nu \xrightarrow{f} N_2\,(a\ ^1\Pi_g) \xrightarrow{g} N + N \qquad \text{(a)}$$

where f is the amount of solar energy absorbed per N_2 molecule per unit time (at the atmospheric height under consideration) within the active waveband and g is the fraction of the excited N_2 (a $^1\Pi_g$) molecules produced per second which undergo dissociation.

In the Mitra process the primary reaction is the production of N_2^+ ions by absorption in the range $\lambda < 795$ A.

$$N_2 + h\nu \xrightarrow{f'} N_2^+\,(X') + e^- \qquad \text{(b)}$$

where f' is the amount of solar energy in the spectral range $\lambda < 795$ A absorbed per N_2 molecule per unit time (at the height under consideration). The nitrogen ions may, in turn, undergo recombination of N_2^+ ions with electrons.

$$N_2^+\,(X') + e^- \xrightarrow{\beta} N\,(^2P) + N\,(^2D) \qquad \text{(c)}$$

where β is the coefficient of dissociative recombination of N_2^+ ions and electrons.

The energy released by the left hand side of (c) is 15.58 ev (first ionization potential of N_2) and that required on the right hand side is the dissociation of N_2 (9.76 ev) plus the energies of excitation

of the two N atoms, 3.56 ev and 2.37 ev, respectively, or a total of 15.69 ev. The difference (15.69 - 15.58 ev = 0.11) 0.11 ev was considered by Mitra to be made up if the N_2^+ (X') ion be in any of the low vibrational levels (v" = 1). Also Bates in a private communication considered the deficiency to be made up if the recombining electron is sufficiently energetic.

Atomic nitrogen may disappear through a three-body collision process

$$N + N + M \xrightarrow{k'} M' + N_2 \qquad (d)$$

or a two-body process

$$N + N \xrightarrow{\alpha} N_2 + h\nu \qquad (e)$$

where k' and α are the coefficients of the recombination processes. These equations give the equilibrium link between the number densities of molecular and atomic nitrogen.

The method of calculation used by the author was a modification of the Penndorf (1949) method for determining the distribution of atomic oxygen in the upper atmosphere. Deb shows in the present paper that the Herzberg and Herzberg mechanism is operative in the height range 70-170 km, and that of Mitra is effective at a much higher height range 200-400 km.

In the 70-170 km height range the dissociation was found to be less than one percent with a maximum distribution of N atoms at an altitude of about 90 km. In the 170-400 km range the dissociation increased from 5 percent at 170 km to about 25 percent at 400 km. In the latter height range there was no maximum distribution. The predissociation process suggested by Herzberg and Herzberg is operative in the 80-100 km region near the E layer of the ionosphere, while the dissociative recombination of N_2^+ ions with electrons (Mitra's process) is effective about 170 km in

the F region. Tables and graphs of distribution with height are included in the paper. There are 17 literature references.

Douglas, A. E., "The Near Ultraviolet Bands of N_2^+ and the Dissociation Energies of the N_2^+ and N_2 Molecules", Can. J. Phys., 30, 302-313, (1952).

The difficulty of obtaining a source of the N_2^+ bands which is relatively free from bands of N_2 was solved in the present investigation by passing a discharge through helium containing a trace of nitrogen in a hollow cathode discharge tube. Fourteen bands of N_2^+ not previously recorded were found and their rotational fine structures analyzed.

The author concludes that the higher value of the dissociation energy of N_2 requires that the $^5\Sigma_g^+$ of N_2 resulting from normal atoms be stable and that this $^5\Sigma_g^+$ predissociate the a $^1\Pi_g$ state. Spectroscopic evidence therefore appears to favor the value of 9.756 for the dissociation energy of N_2. The B $^2\Sigma_u^+$ state of N_2^+ was shown to dissociate at a limit of 70,358 cm^{-1} above the ground state.

Dufay, J., "Investigation of the Forbidden Lines ^2D - ^2P of the Neutral N I in the Absorption Spectrum of the Sun's Atmosphere", Ann. astrophys., 15, 359, (1952).

In this note the author reports the observed intensities of 2 and -2, respectively, of the lines 10407.0 and 10397.6 A in the sun's spectrum. These lines were attributed by Guzit to the forbidden transition ^2D - ^2P of N I. It is stated that the faint line λ10,397.6 A may correspond to the forbidden transition ^2D - ^2P of N I; however the other component (10,407.0 A) of the doublet should have about the same intensity as -2. The author suggests the λ10,407.0 A line is masked by a strong line of unknown origin. Consequently the accurate measurement of equivalent width to determine the number of nitrogen

atoms in the solar atmosphere is impossible.

Dufay, Maurice, "Excitation of the ^4S - ^2D Line of Atomic Nitrogen in the Upper Atmosphere at Twilight", Mem. Soc. Roy, Sci., Liege, 12, 141, (1952).

In the paper Dufay reports that the forbidden N I radiation ^4S - ^2D at λ5199. 1 A has been observed in the twilight sky and also during the night. The line is seldom photographed, but it appeared consistently in the photographs during twilight.

Garstang, R. H., "Multiplet Intensities of the Lines ^4S - ^2D of S II, O II and N I", Astrophys. J., 115, 506, (1952).

This paper reports the calculations of the transition probabilities and intensity ratio of the doublet ^4S - ^2D of S II. Revised transition probabilities and intensity ratios are also included for the ^4S - ^2P doublets of N I and O II.

Gartlein, C. W. and Miss Dora F. Sherman, "Identification of O_2 Bands and Forbidden Nitrogen in Auroral Spectra", Mem. Soc. Roy. Sci., Leige, 12, 187, (1952).

This paper reports the identification of the various features in auroral spectra between 4708 and 5800 A. The work is based upon fourteen spectrograms obtained from 1939 to 1946 by means of a two-prism spectrograph having a camera of 10-cm focus and aperature F/1.65. The dispersion was about 240 A/mm at 5200 A.

One of the features on the plates was the strong peak 5198.1 A which was identified as the forbidden N I. There appeared to be no other

gaseous lines in the range 5196-5202 which would appear in the aurora. It was observed that there was a tendency for the line 5198 A to be strong when the lines at 5003 and 5677.6 are strong. The latter lines were identified as multiplets of N II. These observations were taken to be as evidence of the existence of N I and N II in auroral spectra.

Herman, R., L. Herman, and G. Hepner, "Processes of Emission of the Molecular and Atomic Spectra of Nitrogen Observed in the Light of the Polar Aurora", Trans. Am. Geophys. Union, 33, 489, (1952).

In the present paper the authors have described their recent experiments on the discharge and afterglow spectrum of nitrogen-helium mixture. They state that the spectrum of the polar aurora in the wavelength region 3150 to 9000 A is known to be predominantly that of atomic and molecular nitrogen and oxygen and atomic hydrogen. Reference is made to the laboratory investigations of the radiation of the afterglow spectrum by Kaplan (1932, 1938). Also, Herman and Herman have investigated the afterglow spectrum immediately after the end of the discharge (10^{-2} to 10^{-4} sec.) which the authors call the short-duration afterglow.

With reference to nitrogen lines N I, laboratory investigations revealed that they were very strong in both the discharge and the afterglow. The following mechanism of ion-electron recombination is suggested for their cause.

$$N^{+}\ (2p^{2}\ {}^{3}P_{0}) + e^{-} \rightarrow N^{**} \rightarrow N^{*} + h\nu$$

The ionization potential of N^{+} $(2p^{2}\ {}^{3}P_{0})$ is 29.60 ev and that of N $(2p^{2}\ {}^{4}S^{0})$ is 14.54 ev, giving a total of 44.14 ev. From this the authors conclude that the ionization of nitrogen atoms during the afterglow is a recombination between N^{++} ions and electrons. It is suggested

that an important part of the spectrum of the aurora is emitted after the passage of the exciting particles and is actually an afterglow spectrum.

Herman, R., L. Herman, and G. Hepner, "Short Duration Afterglow of Nitrogen in the Photographic Infrared", Phys. Rev., 86, 570-571, (1952).

Reference is made to Kaplan [Phys. Rev., 42, 807, (1932); 54, 176, (1938)] who first studied the afterglow of long duration (0.1 to 1 sec) which produces the first negative band system $B\ ^2\Sigma - X\ ^2\Sigma$ of N_2^+. Reference is also made to the short duration afterglow (10^{-4} to 10^{-2} sec) in which the same band system is emitted.

The present paper is an extension of the authors' studies of the short duration afterglow of nitrogen into the photographic infrared. An example of the spectrum is shown in Figure 1 of the present paper. The results appear to indicate that the process of excitation of the positive bands is different from the negative bands and atomic lines. It is suggested that the atomic lines may be emitted by ion electron recombination which is relatively more important during the afterglow.

Knuckles, C. F. and J. W. Swensson, "The Spectrum of Lightning in the Region $\lambda 6159 - \lambda 7157$", Ann. geophys., 8, 333, (1952).

The following lists of wavelengths and identifications of the spectrum of lightning are available.

Region	Investigator	Reference
λ 2953- λ4861	M. Dufay	Ann. geophys., 5, 255, (1949)
λ 3835- λ6563	Dufay and Tcheng Mao-Lin	Ann. geophys., 5, 137, (1949)
λ 7424- λ8719	P. D. Jose	J. Geophys. Research, 55, 39, (1950)
λ 7157- λ9078	Petrie and Small	Phys. Rev., 84, 1263 (1951)

The authors in the present paper state that the spectrum of lightning has been rather completely described for the wavelength range λλ 2953-9078 A with the exception of the wavelength interval from λ6563 to λ7157. The subject of the present investigation was to study the latter region. The atoms and molecules have been definitely identified in the spectra of lightning: H, C I, N I, N II, O I, O II, A I, N_2 (second positive), and N_2^+. There is also some evidence for the presence of weak bands due to OH and NH radicals from the investigation by M. Dufay (1949).

The observations reported by Knuckles and Swensson were made during a spectacular lightning storm 9 March 1951 at the McDonald Observatory, Fort Davis, Texas. Two excellent spectrograms were obtained employing the so-called B-spectrograph which consisted of an f - 4 aluminum-on-glass parabolic collimator, a plane aluminum-on-glass grating, and an f - 0.65 Schmidt camera. The authors report the identification of the following constituents for the wavelength region studied.

λ	Extension	Identification
6159	6153-6173	O I
6453	6445-6465	O I
6483	6478-6503	N I
6560	6556-6568	H
6609	---------	N II
6648	6638-6662	N I
6722	6708-6744	N I
7157	7154-7160	O I

The fourth column in the authors' table included the revised multiplet data by C. E. Moore ["A Multiplet Table of Astrophysical Interest", (Revised Edition), Contr. Princeton Observatory, No. 20, (1945)].

Massey, H. S. W. and E. H. S. Burhop, "Electron Collisions in Nitrogen", Electronic and Ionic Impact Phenomena, Oxford, Clarendon Press, p. 263 (1952).

With reference to the production of atomic nitrogen the authors state that there is one important difference between oxygen and nitrogen molecules. This is the failure to observe dissociation of the nitrogen molecule into neutral atoms by electron impact similar to that observed for molecular oxygen.

Reference is made to the experiments of Hughes and Skellet [Phil. Mag., 41, 778, (1921); ibid., 48, 56, (1924)] which showed no decrease in pressure until the electron energy exceeded 17.8 volts. The ionization potential of N_2 is 15.7 volts while the onset potential for the reaction

$$N_2 \rightarrow N + N^+ + e$$

is 22.9 volts. The authors state that observed effects may have been associated with the chemical activity of N_2^+.

Nicholls, R. W., "A Mechanism for Active Nitrogen", J. Chem. Phys., 20, 1040, (1952).

It is stated that the term "active nitrogen" is somewhat loosely applied to the yellow afterglow phenomenon, the Lewis-Rayleigh afterglow. Many mechanisms have been suggested to explain the chemical and physical properties exhibited by the afterglow. Probably no one mechanism can explain all the properties of active nitrogen.

The mechanism discussed in this note involves molecules in vibrational levels of the metastable stage of a $^1\Pi_g$ of N_2.

$$N_2 (a\ ^1\Pi_g) + e(\text{slow}) \longrightarrow N_2 (B\ ^3\Pi_g) + e$$

Nicolet, Marcel, "Effect of Solar Radiation of the High Atmosphere", Ann. geophys., 8, 141, (1952).

This is a comprehensive theoretical discussion on the effect of solar radiation on the high atmosphere. It is stated that to follow the process of absorption and photoionization, a knowledge of the coefficients of absorption and recombination are required. The recombination coefficients will vary with altitude and are difficult to obtain.

With reference to atomic nitrogen Nicolet states that at altitudes between 120 and 150 km the combined effect of X-rays and ultraviolet radiation causes the dissociation of molecular nitrogen. The mechanism of the photodissociation of molecular nitrogen is not clearly understood. It is suggested that the formation of atomic nitrogen is associated with the predissociation of N_2^+ ions which rise rapidly into the ionosphere where the N_2^+ ions are dissociated by electron collisions.

Nicolet, Marcel, "Theoretical Altitudes of the Layers of Night Sky Emissions", Mem. Soc. roy. Sci., Liege, 12, 71, (1952).

In the introduction Nicolet states that the theoretical determination of the altitudes of the layers of night sky emission is essentially based upon two procedures: first, the excitation mechanism of the emission under consideration; and second, the spectral structure of the emission being studied.

With reference to atomic nitrogen the author considers the night sky radiations in the Vegard-Kaplan bands. The following process is assumed.

$$N\,(^4S) + N\,(^2D) \longrightarrow N_2\,(A\ ^3\Sigma)$$

$$N_2\,(A\ ^3\Sigma) \longrightarrow A\ ^1\Sigma + \text{ Vegard-Kaplan band.}$$

This mechanism postulates the existence of a determined number of neutral N atoms and especially of excited $N\,(^2D)$ atoms. Such a process would therefore appear at a high altitude where nitrogen would be dissociated and where the concentration of the excited atoms would be sufficient. The question of the emission of the forbidden transition of N I at λ5200 A is mentioned. If the above hypothesis is correct, the emission of the Vegard-Kaplan bands would certainly take place at a level higher than 150-200 Km.

In the twilight emission that of N I at λ5200 A is essentially due to an excitation by resonance under the influence of solar radiation. The height of this emission was interpreted theoretically by Nicolet to be about 200 km. The appearance of radiation λ5200 A during twilight, when the sun's tangent rays exceed the altitude of 150 km, indicates that the resonance process is admissible. The number of photons emitted per atom per second is of the order of 7.5×10^{-11}, Under these conditions, for a column of 1-cm^2 cross section the number of

photons emitted per second may reach and exceed 10^6 photons/cm^{-2}/sec^{-1} when the concentration of N I above 200 km is of the order of the concentration of O I.

Nicolet, Marcel and P. Mange, "An Introduction to the Study of the Physical Constitution and Chemical Composition of the High Atmosphere", Sci. Report No. 35, Ionospheric Research, The Pennsylvania State College, 15, April 1952.

In this introduction to the study of the physical constitution and chemical composition of the high atmosphere the problem of the dissociation of molecular oxygen is considered in detail with reference to the effect on variable molecular weight and hence temperatures in the upper atmosphere. The authors state that as yet they are not able to obtain directly a quantitative value of the atomic nitrogen concentration. In the model atmosphere discussed in this report it was assumed that the partial dissociation which certainly exists does not affect the concentration of N_2 molecules. As a result the atomic nitrogen concentration is only a small fraction of the total concentration where the diffusion effects begin.

Tables XII and XIII in the report give the maximum values of oxygen and nitrogen concentrations in the exosphere from 550 to 1000 km based on the temperatures 2500 and 1500°K at the critical level. The authors mention in conclusion that in the polar auroras lines of neutral and ionized atomic nitrogen have been observed by Barbier, Bernard, Gartlein, Meinel, Petrie, and Vegard. Dufay and Götz have found at lower latitudes the forbidden lines of N I at λ5200 A in several auroras.

A discussion is given of the observance of the N_2^+ bands in the airglow spectra. It is concluded that the distribution of N_2^+ molecules as a function of height at twilight and dawn does not correspond

to the deduced density distribution of the photoionization process. Two hypotheses are given concerning N_2^+ heights and diffusive transport from which certain deductions may be made about the ionosphere.

The authors state that maximum photoionization of N_2 cannot occur below 150 km if nitrogen is not dissociated. Two mechanisms are suggested. One is that N_2 is dissociated at 150-200 km and the N_2^+ bands in auroras are due to an association process.

$$N^+ + N \rightarrow N_2^+ + h\nu$$

This process requires a vertical transport of N_2^+ during an aurora for N_2^+ to reach altitudes of 800-1000 km. The other is that N_2 is not dissociated at 150-200 km. When N_2^+ is produced it is immediately destroyed by a dissociative process.

$$N_2^+ + e^- \rightarrow N + N$$

The authors conclude that in the exosphere the atomic nitrogen concentration is of the same order as the molecular nitrogen concentration. In the 300-150-km region the absorption of solar radiation of atomic nitrogen is negligible compared with the absorption of molecular nitrogen. From these theoretical deductions atomic oxygen is considered the principal source of electrons in the F_1 and F_2 regions, molecular nitrogen being unimportant in electron production because recombination is too rapid.

Nicolet, M. and R. Pastiels, "Atomic and Molecular Nitrogen in the High Atmosphere", Mem. Soc. roy. Sci., Liege, 12, 147, (1952).

The authors state that evidence for the presence of atomic nitrogen in the upper atmosphere is given by observations of N I and N II lines in auroral spectra and also by certain theoretical considerations concerning the formation of the ionized layers. The presence of N_2^+ bands

in the auroral rays would seem to indicate that the N_2 molecule is not completely dissociated. The authors give two extreme conclusions which may be possible. a. N_2 is dissociated only when the auroral effects appear, and the normal composition of the heterosphere is given by O and N_2. b. Atomic nitrogen is a normal element of the heterosphere coming from a special reaction. Observation of the N_2^+ bands indicates only the ionized molecule.

The principal association mechanism is

$$N + N + M \rightarrow N_2 + M$$

The authors state that since the recombination coefficient is of the order of 10^{-32}, the time required for recombination can be calculated. Thus below 100 km the effect of a complete dissociation is negligible after one day, but at 200 km the recombination does not appear (many years) and the atomic nitrogen is a permanent element.

To account for the presence of N_2^+ the following recombination process must occur,

$$N + N^+ \rightarrow N_2^+ + h\nu$$

accounting for N_2^+ in the F region. According to Bates the recombination coefficient is of the order of 3×10^{-17} for this reaction.

The twilight effect of the atomic nitrogen line at $\lambda 5200$ is briefly mentioned. It is stated that for $\lambda 5200$ the number of photons emitted (without collisional de-activations) is 7.5×10^{-11} per atom-sec, while for the red line of O I the number of photons is 7.25×10^{-10}. Thus if the nitrogen atoms in the F region are as abundant as the oxygen atoms, the observation of a twilight effect at $\lambda 5200$ A should be possible. The authors conclusions appear to corroborate the observations of Courtes (1950) and to give strong indications for the permanent presence

of the λ5200 A line. Ionized atomic nitrogen is explained by X-ray ionization.

Petrie, W. and R. Small, "The Auroral Spectrum in the Wavelength Range 3300-8900 A", Astrophys. J., 116, 433, (1952).

The authors discuss the wavelengths and identifications of the auroral features from spectra obtained with a new spectrograph constructed in 1951 at the University of Saskatchewan. In Tables 3 and 4 of the paper the N I and N II lines in the auroral spectrum are listed.

It is stated that the forbidden lines at λ5198 and λ5201 appear only in high altitude displays and that they were secured in all the spectra. There was a strong line at λ6483 which could be interpreted as due to the N I transition $2p^2 3p\,(^4D^0) \rightarrow 2p^2 4d\,(^4F)$ excitation potential 13.62 ev; however it probably belongs to the spectrum of N II owing to the greater intensity of N II lines in the aurora. In Table 3 there are given the various wavelengths and excitation potentials corresponding to several multiplet transitions.

Petrie, W., "Forbidden Line of N I in the Aurora", Phys. Rev., 87, 1002, (1952).

Reference is made to the paper by Petrie and Small [Astrophys. J., 116, 433, (1952)] in which they noted that the forbidden O I and N I lines are stronger than the permitted lines of the same atoms, while in the case of O II and N II permitted lines are present, but the forbidden lines of these ions are either very weak or absent.

The present paper discusses the more recent and stronger spectrograms obtained in the regions of the forbidden lines of O II and N II. The following observation and definite statement was made. The weakness of the forbidden O II and N II lines was considered to be due to the

fact that a single process (i.e., ionization and excitation from the low levels of O I and N I)populates the levels involved. The strong forbidden lines of the neutral atoms are excited by several processes.

Spitzer, Lyman, Jr., "The Terrestrail Atmosphere above 300 Km", The Atmospheres of the Earth and Planets, Revised Edition, (Kuiper, Gerald P., Editor), The University of Chicago Press, Chicago, Illinois, pp. 217-219, 1952.

With reference to the composition of the atmosphere in the region 100-300 km Spitzer considers briefly the evidences for the presence of atomic nitrogen. Brief reviews are given of the following studies. Wulf and Deming (1938) and Ta-Your Wu (1944) estimated the extent of dissociation of N_2 by ultraviolet radiation of wavelength less than 1000 A. Dissociation was found to occur between 100 and 300 km. Herzberg (1945) suggested predissociation of N_2 caused by radiation below 1400 A. Chapman and Price (1936) considered that absorption less than 800 A would lead to ionization rather than dissociation, and that predissociation was possible only from excited states but not for transitions from the ground state. Nicolet (1947) suggested that nitrogen atoms are produced from the dissociation of N_2O, the latter being formed from atomic oxygen and molecular nitrogen. Experimental evidence for the existence of atomic nitrogen in abundance in the upper atmosphere has been furnished by Bernard (1938); by Dufay and Tcheng Mao-Lin (1941); and by Stebbins, Whitford, and Swings (1945). Spitzer concludes from this brief survey that an appreciable fraction of nitrogen is atomic, at least at 300 km; also that dissociation cannot be complete at 300 km since N_2 bands have been observed from auroras at much higher altitudes.

Stanz, Dietrich, "The Lowest of the Ionized Lyaers of the Upper Atmosphere", Tellus, 2, 150-157, (1952).

The author includes a list of photochemical processes (dissociation and ionization) acting upon atmospheric oxygen and nitrogen.

(a)	$N_2 + h\nu \rightarrow N_2^+ + e^-$	$\lambda \leq 661$ A	F_2 layer
(b)	$O + h\nu \rightarrow O^+ + e^-$	$\lambda \leq 667$ A	F_2 layer
(c)	$O + h\nu \rightarrow O^+ + e^-$	$\lambda \leq 732$ A	F_2 layer
(d)	$O_2 + h\nu \rightarrow O_2^+ + e^-$	$\lambda \leq 765$ A	E layer
(e)	$N_2 + h\nu \rightarrow N_2^+ + e^-$	$\lambda \leq 795$ A	E layer
(f)	$O + h\nu \rightarrow O^+ + e^-$	$\lambda \leq 910$ A	F_1 layer
(g)	$O_2 + h\nu \rightarrow O_2^+ + e^-$	$\lambda \leq 1010$ A	D layer
(h)	$O_2 + h\nu \rightarrow O^* + O$	$\lambda \leq 1330$ A	O atom layer D layer
(i)	$O_2 + h\nu \rightarrow O^* + O$	$\lambda \leq 1715$ A	O atom layer
(j)	$O_2 + h\nu \rightarrow O + O$	$\lambda \leq 2424$ A	O_3 layer

In regard to the formation of the D layer the author gives the theory of A. and E. Vassy (1948), which ascribes the formation to the ionization of Na in the upper atmosphere. According to the theory of the Vasseys, Lyman alpha is consumed above an altitude of 100 km so that the formation of the D layer would not be possible by this method. Radiation of wavelength greater than 1800 A is responsible for the ionization of Na. The D layer usually shows a cloudy structure which might be identical with Na-clouds. However Penndorf (1947) from calculations of the border of the ozone shadow found that the twilight luminescence due to sodium came from the E layer (110-120 km).

Vegard, Lars and E. Tönsberg, "Results from Auroral Spectrograms obtained at Tromsö during the Winter 1950-1951", Geofys. publ., Oslo, 18, No. 8, (1952).

The results contained in this paper are collected in an extensive table of spectral lines and bands in the auroral luminescence. The wavelengths and interpretations are given.

With reference to atomic nitrogen the authors state that one of the forbidden N I lines $({}^2D \rightarrow {}^2P)$ lies in the infrared and that the line N I $({}^4S \rightarrow {}^2P)$ (3466 A) appears in the auroral spectrum. The doublet N I $({}^4S_{3/2} \rightarrow {}^2D_{5/2,\,3/2})$ (5201 A, 5198 A) is not separated, but coincides with the auroral line 5199.5 A. The line 5199 A on the Oslo spectrogram is more than twice as strong as the band head of 5227 A. A latitude effect of greatly enhanced lines for the forbidden N I was found in passing towards lower latitudes. The latitude effect of enhancement towards lower latitudes has not been investigated for the forbidden N I line 3466 A.

Vegard, Lars, "Recent Advances in Auroral Spectroscopy and in our Knowledge of the Upper Atmosphere", Ann. geophys., 8, 91, (1952).

This paper is a communication by Vegard presented to the Assembly of the International Union of Geodesy and Geophysics meeting at Brussels (1951). Reference is made to the author's communication to the Oslo meeting of August 1948 in which Vegard outlined some essential properties of the upper atmosphere inferred from his investigations of the auroras.

The author states that physical conditions existing in the auroral region differ essentially from those of the lower atmosphere. The

barometric height formula breaks down and is not applicable to this region. It is suggested that the matter in the upper atmosphere is transformed by solar activity radiation, and as a result the auroral region takes the shape of a coronal structure similar to that of the sun.

Vegard briefly describes his theory of the upper atmosphere. The bundles of electric rays producing the auroral luminescence are considered to be a mixture of fairly high-speed electrons with ions of great specific charge which are mainly protons. The protons neutralize the ray bundles preventing the electrons from being spread out in all directions. This theory was advanced by Vegard in 1916 [Ann. Phys., 4, 50, p. 853, (1916)].

The author states that at the time of the Oslo meeting about 170 auroral lines had been observed and measured. Using an improved spectrograph, which was first used on the night of 23-24 February 1950 at Oslo and later taken to the Auroral Observatory at Tromsö, the number of lines and vibrational bands observed from the auroral luminescence has been found to be about 500. The following table of classification is included in the paper which summarizes the author's observations.

Atomic Lines		Vibrational Bands			
Origin	N_c	System	N_c	System	N_c
O I	67	N_2 1 N	30	O_2 1 N	26
O II	158	N_2 2 N	28	O_2 2 N	4
N I	173	N_2 1 P	57	O_2 S.R.	47
N II	132	N_2 2 P	32	NO	15
H	3	N_2 V.K.	43		

The notation N_c is the number of auroral lines, 1 N is first negative, 2 N is second negative, 1 P is first positive, V. K. is Vegard-Kaplan bands, and S. R. is Schumann-Runge bands.

With reference to the atomic lines in addition to the hydrogen lines and the yellow sodium line 5893 A, nearly all the remaining were identified with lines from neutral and ionized atoms of oxygen and nitrogen. Among the great number of N I lines the doublet (5202.5 A, 5197 A) having a mean wavelength of 5199 A and originating from the forbidden transition N I $^4S_{3/2} \rightarrow {}^2D_{5/2,3/2}$ was observed.

Weissler, G. L., Po Lee, and E. I. Mohr, "Absolute Absorption Coefficients of Nitrogen in the Vacuum Ultraviolet", J. Opt. Soc. Am., 42, 84, (1952).

Reference is made to the study of the absorption of the hydrogen line 1215.7 A for air and its principal component gases by Williams [Nature, 145, 68, (1940)]. In this study Williams found that nitrogen is transparent in layers up to 3.2 mm (N P T), while a layer of only about 0.05 mm of water vapor decreases the intensity by one-half and oxygen decreases it by the same amount in layers of 0.5 mm.

The purpose of the work reported in the present paper was to investigate the absorption by N_2 in the vacuum ultraviolet. Apparatus and experimental procedures are discussed in detail. The results of the absorption coefficients, k, in nitrogen were obtained for 88 wavelengths between 300 A and 1300 A. These are listed in Table I in the paper.

It was found that absorption near 1300 A was very low, less than 10 cm^{-1} which supported the fact of an "air-window" in this region. In the region between 1300 and 1000 A no k-values were found to be greater than 150 cm^{-1} for about 30 source lines measured. Below 1000 A the values of the coefficients increased to several hundred and a molecular

absorption band was always found. Low k-values were still found at 832 A, indicating that in the region from 1300 to 800 A continuous absorption was small, of the order of 50 to 150 cm^{-1}. Below 800 A no small coefficients were found, suggesting an absorption continuum superimposed by molecular band absorption. Between 796 A and 661 A the k-values were larger than 600 cm^{-1}. Below 661 A the absorption decreased to $k = 90\ cm^{-1}$ at 303 A.

1953

Banerji, R. B., "Recombination Coefficient in the F-Regions: A Possible New Process of Ionization of Nitrogen Molecules", Nature, 172, 953, (1953).

Reference is made to the papers by Bates and Massey [Proc. Roy. Soc. (London), A 192, 1, (1947); and ibid., A 187, 261, (1946)] in which they show that the high day-time rate of disappearance of electrons in the E and F regions of the ionosphere cannot be explained by the negative-ion formation theory in the second reference above.

The author states that the ionized constituent in the F region is the O^+ ion. For the dissociative recombination mechanism to be operative, the atomic ions must give rise to molecular ions. The atmospheric constituents in the F region are nitrogen molecules and oxygen atoms. The following process is considered highly probable.

$$O^+ + N_2\,(A\ ^3\Sigma_u) \longrightarrow N_2^+ + O\,(^1S)$$

If the ionization potential of O is 13.55 ev and the energy of the $O\,(^1S)$ state is 4.17 ev, then 9.38 ev of energy is released. This energy is sufficient to ionize the nitrogen molecule in the $A\ ^3\Sigma_u$ state (6.14 ev), since the ionization potential of N_2 is 15.51 ev.

Assuming a transfer coefficient of 10^{-11} [Bates and Massey (1947)] the concentration of excited nitrogen molecules is 10^7 to explain the recombination coefficient in the F_2 layer where the concentration of nitrogen molecules is 5×10^8. As a result only 2 percent of the molecules need be excited. The author considers such a percentage not improbable. This process is considered to be operative during the daytime or as long as the concentration of excited nitrogen molecules is large. The process also shows how solar radiation in the visible spectrum may be istrumental in ionizing nitrogen molecules if positively charged particles are present.

Barbier, Daniel, "Comparison of the Spectra of Comets and of the High Atmosphere", Mem. Soc. Roy. Sci., Liege, 13, 303, (1953).

This is a paper presented at the Fourth International Colloquium on Astrophysics held in Liege, 19-21 September 1952. The mechanism of excitation of certain radiations in the spectra of comets at close approach to the sun is compared with the lines and bands of those in the night sky and auroral emissions. In addition to the lines and bands of such atmospheric constituents as Na I, O I, OH, observations on the excitation of N_2^+ are discussed.

Bauer, Ernest and Ta-You Wu, "Origin of the E Layer of the Ionosphere", Phys. Rev., 92, 1101, (1953).

This is a comprehensive paper on the photoionization of molecular oxygen and the E Layer. The calculations are based on the work of Moses and Wu on the distribution of molecular and atomic oxygen in the atom-molecule region. The authors conclude that both the observed height and the value of the peak electron density can be accounted for satisfactorily.

The ionization of atomic oxygen and the F_1 layer is also discussed with reference to the following mechanisms.

$$N_2 + h\nu \rightarrow N_2^+ + e^-, \qquad \sigma_N = 10^{-17}\ \text{cm}^2 \text{ at } 15.5 \text{ ev}$$

$$N_2^+ + e^- \rightarrow N' + N'', \qquad \sigma_N = 4 \times 10^{-9}\ \text{cm}^3\ \text{sec}^{-1}$$

The maximum electron density at noon was shown to be expressed as follows:

$$[e]^2 = q_1 [O] / \alpha_1 + q_N [N_2] / \alpha_N$$

The effective recombination coefficient is given by

$$\alpha_{r_1} \left\{ 1 + \frac{q_N [N_2]}{q_1 [O]} \right\} \frac{[O^+]}{[\ell]} = \alpha_N \left\{ 1 + \frac{q_1 [O]}{q_N [N_2]} \right\} \frac{[N_2^+]}{[\ell]}$$

Calculations of $q_N [N_2]$ and $q_1 [O]$ at the heights of the F_1 layer (200 km) based on the three-body association model of Moses and Wu (1953) and on the assumption of linear rise of temperature with altitude between 100 and 200 km

give $q_N [N_2] / q_1 [O] \sim 1/160$ at 200 km. The authors conclude that at this altitude the contribution of the electron density comes predominantly from the oxygen atoms; the rate of recombination is determined essentially be that between O^+ and electrons.

Brook, Marx, "New Studies of Nitrogen Afterglows", Phys. Rev., 92, 1079, (1953).

This is an abstract of a paper presented before the American Physical Society held 2-5 September 1953 at Albuquerque, New Mexico. A description is given of a new flow system to mix the nitrogen afterglow with a rare gas downstream from the discharge. Both the Cario-Kaplan

and the molecular ion theory of Mitra are shown to be inadequate to account for the nitrogen afterglow. It is suggested in the present paper that the most probable mechanism is an atomic recombination process in a three-body collision. There is a transition from the $^5\Sigma$ to the B $^3\Pi$ state.

$$[N + N \rightleftarrows N_2 \ (^5\Sigma)] + N_2 \rightarrow N_2 \quad (B\ ^3\Pi) + N_2$$

$$N_2 \ (B\ ^3\Pi) \rightarrow N_2 \ (A\ ^3\Sigma) + h\nu$$

Chamberlain, Joseph W. and Norman J. Oliver, "Atomic and Molecular Transitions in Auroral Spectra", J. Geophys. Research, 58, 457, (1953).

In this paper the authors have listed in three tables those identifications which they consider to be well established in auroral spectra. Table 1 contains a list of permitted atomic lines in auroras, Table 2 gives forbidden atomic lines in auroras, and Table 3 gives molecular bands in auroras. With reference to the N I 3466 A line reported by Bernard (1939) the authors consider this radiation as identified. The auroral N II transition λ 5755 reported by Petrie (1952) and identified on spectra from observations at Saskatoon, Canada is also considered as definitely identified.

Curtis, J. P. and Wm. A. Rense, "A New Method of Measuring Absorption Coefficients in the Extreme Ultraviolet", Astron. J., 58, 213, (1953).

The authors report the use of photomultiplier tubes coated with sodium salicylate for a method of measuring absorption coefficients in the extreme ultraviolet. Absorption coefficients of air and of nitrogen were measured from 150 to 900 A.

Dufay, Maurice, "Study of Emission from Ionized Molecules and Neutral Atoms of Nitrogen at Twilight", Ann. phys., 8, 813, (1953).

This report gives the results of systematic spectrographic observations made at different seasons and over a period of years. The study was made of the light from the evening and morning sky and had for its purpose the determination of the intensities of the first negative band system of N_2, (0,0) and (0.1), and the forbidden N I lines ($^4S \rightarrow {}^2D$) at 5199 A.

The results obtained for atomic nitrogen show that the doublet 5197.8 and 5200.2 A had variable intensity, being weaker at dawn, with maximum intensity during summer twilight. The results also indicate a fluorescent excitation by direct absorption of solar radiation of wavelength 3466 A at an approximate altitude of 120 km.

Dufay, Maurice, "Intensity of the ^4S - ^2D Line of Atomic Nitrogen at Twilight", Compt. rend., 236, 2160, (1953).

This was a study of the twilight emission of atomic nitrogen at the wavelength 5199 A (^4S - ^2D). Intensity comparison of this line (5199 A) with that of O I at 5577 A indicated a mean intensity for the atomic nitrogen emission of about 1.5×10^7 quanta cm^{-2} sec^{-1} vertical cross-section of atmosphere. The line 5199 A was attributed to the forbidden transition ^4S - ^2D of atomic nitrogen. The emission is not correlated with geomagnetic disturbances. The relation to excitation by fluorescence is also considered.

Erb, D. S., J. P. Curtis, and Wm. A. Rense, "Ultraviolet Absorption in Air from 630 to 1670 A", Astron. J., 58, 214, (1953).

In this note to the Astronomical Journal the authors announce their

photographic study of the absorption coefficients of 36 emission lines of highly ionized oxygen, nitrogen, and silicon at pressures of 0.22, 0.12 and 0.017 mm of mercury. The instrumentation included a 1-meter grazing incidence vacuum spectrograph. A capillary discharge in air was used as source. Mass absorption coefficients were determined for each wavelength and pressure. The authors report no evidence of any systematic change in a coefficient with pressure. There was a region of strong absorption between 1300 and 1700 A as well as a window between 1000 and 1300 A.

Hoeffner, Erik, "Chemical Activation of Hydrogen, Nitrogen and Oxygen by Glow Discharge", Tek. Tidskr (Stockholm), 83, 573, (1953).

This paper is a review of luminous discharge in gases. The chemical reactions of hydrogen, oxygen, and nitrogen involved are also considered.

Jackson, D. S. and H. I. Schiff, "Mass Spectral Investigation of 'Active' Nitrogen", J. Chem. Phys., 21, 2233, (1953).

A study of the nitrogen afterglow was undertaken with the aid of a mass spectrometer in order to determine the composition of "active" nitrogen. The purified nitrogen was subjected to a condensed discharge and afterwards pumped through a conventional diffusion and rotary pump. A small sample of the gas stream was continuously sampled into the mass spectrometer.

When the discharge tube was excited it was found that the ion intensity corresponding to mass 28 decreased while the intensity from mass 14 increased. This suggested the presence of atomic nitrogen. The value of the ratios of the ion intensities for mass 28 and mass 14 are shown in Table I of the paper for different pressures and electron energy. It was concluded that the actual value of the appearance potential

was necessary before positive identification could be made.

Jones, A. Vallance, D. M. Hunten, and G. G. Shepherd, "Rotational Temperatures of Auroral N_2 Bands", Astrophys. J., 118, 350, (1953).

The authors state that there is a discrepancy between the temperature of certain regions of the upper atmosphere derived from the intensity distribution of the rotational fine structure of the N_2 bands of the aurora and temperatures measured by other methods. The results reported in this note were obtained from a microphotometer tracing of 0-0 N_2^+ at 3914 A.

The spectrum was obtained from arc and band features during an auroral display on the night of 3 April 1953. By 2-station photography the height of typical features was found to be 100-120 km. The estimated temperature was 330°K as compared to the Rocket Panel temperature 214°-330°K for these heights.

Kallmann, H. K., "Physical Properties of the Atmosphere between ~80 Km and ~ 250 Km", J. Geophys. Research, 58, 209, (1953).

The latest rockets fired at White Sands by NRL according to Hulbert reached heights of 160 km and in one case of approximately 220 km. To obtain the temperature corresponding to the measured pressure or density at any particular height, the scale height is determined from the well-known barometric equation

$$dP = -g\rho dh \qquad \text{(a)}$$

or

$$\frac{dP}{P} = -\frac{Mg}{RT}\,dh = \frac{1}{H}\,dh \qquad \text{(b)}$$

where P is the pressure, g the acceleration due to gravity, h the height of the atmosphere, M molecular weight, R the gas constant, T the temperature, and $H = RT/gM$ = scale height. If the scale height is known the degree of accuracy obtained in the temperature depends on the accuracy with which M, the molecular weight, is known.

Generally it is assumed that the molecular weight does not change below 80 km. Between 80 and 120 km the incoming radiation is absorbed by the oxygen molecule causing dissociation into atomic oxygen with the result that the molecular weight will decrease. The number of quanta absorbed per unit volume is small at about 130 km and increases rapidly with decreasing height. At about 100 km it reaches a maximum and decreases slowly to become more or less constant after about 10 km.

The region of dissociation of molecular nitrogen is uncertain. Reference is made to Nicolet and Pastiels (1952) who reported evidence for the presence of atomic nitrogen obtained from observations of the lines of N I and N II in the auroral spectra and also from theoretical considerations of the formation of ionized layers. The mechanism for the formation of the observed N_2^+ bands is as follows.

$$N + N^+ \rightarrow N_2^+ + h\nu \qquad \text{(c)}$$

This mechanism requires the presence of neutral and ionized nitrogen atoms in the F_1 region. The region of dissociation of molecular nitrogen is assumed to be between about 150 km and 250 km ± 50 km. The dissociation of nitrogen also causes a decrease in molecular weight with height. There will be a region of maximum absorption for nitrogen as is the case for oxygen. The absorption and recombination coefficients are not known so well for nitrogen as for oxygen.

The author gives the following parameters which are known with a fair degree of accuracy: temperatures up to 80 km; variation of pressure

with altitude up to about 100 km; variation of density with altitude up to about 160 km; and qualitatively, the variation of molecular weight with altitude in the two regions where dissociation of molecular oxygen and nitrogen occur. The following assumptions are made in order to obtain the molecular weight as a function of temperature and of height. (a) O_2 dissociates in the region between 80 and 120 km. (b) N_2 dissociates in the region 130 and 250 km.. (c) The temperature and pressure at the datum level (80 km) are known and the lapse rate is 2.5°K per km. (d) The fractional change in concentration is given by the expression,

$$\frac{dC\left[O_2 \text{ or } N_2\right]}{C\left[O_2 \text{ or } N_2\right]} = -k_1 dh \tag{d}$$

Where C is the concentration of molecular oxygen or nitrogen at any height, and k_1 is a concentration coefficient equal approximately to $1.93 \times 10^{-6}\ cm^{-1}$ for O_2 and $0.98 \times 10^{-6}\ cm^{-1}$ for N_2.

The concentration can be expressed in terms of molecular weight as follows:

$$M_1 = \frac{n(N_2)\ M(N_2) + \left[n(O_2) - X_1\right]\ M(O_2) + 2X_1 M(O)}{\left[1 + X_1\right]} \tag{e}$$

where M_1 is the mean molecular weight of air in the region where oxygen dissociates; X_1 is the number of moles of oxygen dissociated; $M(N_2)$, $M(O_2)$, and M(O) are the molecular weights of nitrogen, diatomic oxygen, and atomic oxygen, respectively; and $n(N_2)$, $n(O_2)$, and N(O) are the corresponding fractions of the constituents present. Expressing the concentration of molecular oxygen in terms of the partial pressures

$$C(O_2) = p/RT \tag{f}$$

using the relation

$$\frac{p}{RT} = \frac{X(O_2)P}{RT} = \frac{\left[n(O_2) - X_1\right]P}{RT\left[1 + X_1\right]} \tag{g}$$

$$\left.\begin{aligned} &\text{then } C(O_2) = \frac{\left[n(O_2) - X_1\right]P}{RT\left[1 + X_1\right]} \quad \left(\frac{\text{moles}}{\text{cm}^3}\right) \\ &\text{or } N_A C(O_2) = N(O_2) \quad \left(\frac{\text{No.}}{\text{cm}^3}\right) \end{aligned}\right\} \tag{h}$$

where p is the partial pressure of molecular oxygen; P is the total pressure of the mixture;

$$X(O_2) = \frac{\left[n(O_2) - X_1\right]}{\left[1 + X_1\right]} = \text{mole fraction of } O_2; \text{ and}$$

N_A (eq. h) is Avogadro's number. Solving equation (d) for the mole fraction and assuming that air consists of 79% nitrogen and 21% oxygen, equation (h) becomes

$$C(O_2) = \frac{0.042\ P}{RT}\ (M_1 - 23.8) \tag{i}$$

The author then finds the change of concentration with respect to height to be

$$\frac{dC(O_2)}{dh} = \frac{0.042\ P}{RT}\left[\frac{dM_1}{dh} + \frac{(M_1 - 23.8)}{P}\ \frac{dp}{dH} - \frac{(M_1 - 23.8)}{T}\ \frac{dT}{dh}\right] \tag{j}$$

If the change of pressure with respect to height is eliminated by barometric equation (b) and the change of temperature with height replaced by the lapse rate, then the fractional change in concentration with height in terms of molecular weight, temperature, and height becomes

$$\frac{dC(O_2)}{C(O_2)} = \frac{dM}{M - 23.8} - \left[\frac{Mg}{RT} + \frac{\alpha}{T} \, dh \right] \qquad (k)$$

Equating (k) to (d) one obtains the change in molecular weight with height.

$$\frac{d\,M_1}{\left[\frac{M_1 - 23.8}{T}\right]\left[\frac{M_1 g}{R} + \alpha - k_1 T\right]} = dh \qquad (l)$$

Where $T = T_o + \alpha\,(h - h_o)$ and T_o is the temperature at the datum level = 190°K, α = lapse rate (dT/dh), and h_o is the datum level (80 km). While equation (l) determines the molecular weight of the atmosphere where oxygen dissociates, the following equation determines the molecular weight of the atmosphere in the region where nitrogen dissociates: (m)

$$\frac{dM_2}{dh} = \left[\frac{M_2 - 14.4}{T}\right] \left[\frac{M_2 g}{R} + \alpha - k_2 T\right] \qquad (n)$$

where M_2 is the mean molecular weight of the atmosphere above the new datum level (130 km) and 14.4 is the molecular weight of the atmosphere when nitrogen has been completely dissociated. The constants k_1 and k_2 in (l) and (n) were determined by setting $dM/dh = O$ at the datum levels, that is, at 80 km and 130 km respectively; the values obtained are $k_1 = 1.925 \times 10^{-6}\ cm^{-1}$ and $k_2 = 0.98 \times 10^{-6}\ cm^{-1}$.

The analytical integration of (l) and (n) is rather difficult, but a solution can very easily be obtained from a differential analyzer or by numerical integration. Once the molecular weight is obtained the scale height can be calculated from the relation

$$H = RT/Mg \qquad (o)$$

From a plot of $-1/H$ vs height $\ln P/P_o$ can be obtained by graphical integration; P is the total pressure at a given height and P_o is the known pressure at the datum level. The density is obtained from the equation of state $\rho = PM/RT$ and the number density is obtained from the relation $n = P/kT$ where k is Boltsmann's constant.

Meinel, A. B., "Origin of the Continuum in the Night Sky Spectrum", Astrophys. J., 118, 200, (1953).

The author states that the spectrum of the light of the night sky appears to be dominated in the blue and violet by a strong continuum upon which a few emissions are superimposed. It is suggested that the continuum of the airglow spectrum in the 3700-4800 A region may be more completely due to starlight than has hitherto been supposed.

The emission at 3914 A in the airglow was identified as N_2 (0,0) band superimposed on the stellar continuum to the violet of the K line. Two explanations may be given for the line: either it is due to the twilight airglow, or it represents a true permanent "aurora" due to optical excitations of the air by the flux of cosmic rays.

Mitra, A. P., "A Tentative Model of the Equilibrium Height Distribution of Nitric Oxide in the High Atmosphere and the Resulting D Layer", Sci. Report No. 46, Ionospheric Research, The Pennsylvania State College, 15 May 1953.

With reference to the presence of atomic nitrogen in the atmosphere Mitra cites various observations of different investigators. Bernard (1939) estimated that the N I atoms in the ^2P state were four times less numerous than the O I atoms in the ^1S level at the base of the aurora, while they were

three times more numerous at the top of the aurora. Dufay (1943) found the number of N I (^2D) atoms was seven times larger than the number of O I (^1D) atoms. Mitra concludes that there is much evidence for the presence of atomic nitrogen in the auroral region. Reference is also made to the discovery by Courtes (1950) and to Dufay (1951) who found the radiation λ5199 in the airglow spectra.

The following number densities for N I are given in the report: $1 \times 10^{11}/cm^3$ if the emission originates at an altitude of 95 km, and $1 \times 10^{10}/cm^3$ if the emission originates at 70 km. The two processes of photodissociation of molecular nitrogen suggested in recent years are the Herzberg-Herzberg process and the Mitra process. In the Herzberg-Herzberg process predissociation of N_2 molecules occurs by absorption in the Lyman-Birge-Hopfield band in the λλ1150-1250 A spectral range.

$$N_2 + h\nu \xrightarrow{f} N_2(a\ {}^1\Pi_g) \xrightarrow{g} N + N$$

where f is the amount of solar energy absorbed per N_2 molecule per unit of time at the height level of the active absorption band in the atmosphere and g is the fraction of the excited $N_2(a\ {}^1\Pi_g)$ molecules produced per second which undergo dissociation.

The process suggested by S. K. Mitra (1951) involves the formation of nitrogen atoms by dissociative recombination of N_2 ions and electrons.

$$N_2 + h\nu \xrightarrow{\lambda < 795\ A} N_2^+ (X') + e^-$$

$$N_2 + (X') + e^- \longrightarrow N(^2P) + N(^2D)$$

Reference is also made to the paper by Deb (1952). Deb concluded that the two processes are operative at different levels in the upper atmosphere. Below the height of 170 km the Herzberg-Herzberg process is the important one, while above this level the process by Mitra predominates.

In the present report Mitra gives in Figure 6 the vertical distribution of atomic nitrogen based on the two distribution of N_2O depending upon whether O_3 and N_2 are the parent substances

$$O_3 + N_2 \rightarrow N_2O + O_2$$

or if atomic oxygen and N_2 are the parent substances.

$$N_2 + O + M \rightarrow N_2O + M$$

The distribution curve derived by Deb differs from those of Mitra in that Deb did not employ certain reactions involving the production and disappearance of atomic nitrogen. The effect of the solar zenith angle on the height distribution is also discussed. On the assumption that the $N(^2D)$ atoms involved are formed by solar radiation by the following mechanism :

$$N(^4S) + h\nu \rightarrow N(^2D)$$

$$N(^4S) + h\nu \rightarrow N(^2P)$$

$$N(^2P) \rightarrow N(^2D) + h\nu$$

the required number of nitrogen atoms is about $5 \times 10^{16}/cm^2$ column, i.e., about $1 \times 10^{10}/cm^3$.

Mitra, A. P., "Atomic Nitrogen as a Constituent for Region F_1", Sci. Report No. 53, Ionospheric Research, The Pennsylvania State College, 10 November 1953.

In the introduction Mitra points out the absence of a single photo-dissociation process for molecular nitrogen, N_2, analogous to that of O_2 in the upper atmosphere. The objections to the existence of atomic nitrogen as a constituent of the upper atmosphere have been removed in

recent years by the discovery of atomic nitrogen lines in the airglow by Courtes (1950) and Dufay (1951). Also atomic nitrogen may be produced appreciably by the dissociation recombination process [Mitra, S. K. (1951) and Bates (1950)].

The dissociation recombination mechanism by Mitra is expressed as follows.

$$N_2 + h\nu \xrightarrow{\lambda < 795\ A} N_2^+(X') + e^- \qquad \text{(a)}$$

$$N_2^+(X') + e^- \longrightarrow N(^2P) + N(^2D) \qquad \text{(b)}$$

Atomic nitrogen is produced at low altitudes by the Herzberg and Herzberg (1948) process.

$$\left\{ \begin{array}{l} N_2 + h\nu \xrightarrow{1150\text{-}1250\ A} N_2\ (a\ ^1\pi_g) \\ N_2\ (A\ ^1\pi_g) \longrightarrow N + N \end{array} \right\} \qquad \text{(c)}$$

Nicolet (1952) has suggested that N_2^+ may be formed by the mechanism.

$$N + N^+ \longrightarrow N_2^+ \qquad \text{(d)}$$

The author states that the purpose of the present report was to examine the problem of N_2-dissociation and also the problem of ionization of the resulting nitrogen atoms. It is shown in the report that atomic nitrogen appears to contribute partly to the ionization of Region F_1. Some of the topics considered are: general considerations, upper atmospheric characteristics, absorption coefficients, and intensity of solar radiation.

In regard to atomic nitrogen it is formed mainly by the dissociative process, equations (a) and (b), and by the Herzberg-Herzberg process, equation (c). Reference is made to Deb (1952) who showed that at heights of 150 km or above only the dissociative recombination process is operative, and as a result Mitra in the present report considers only this latter process.

Nitrogen atoms may disappear through the following processes [Mitra, Indian Jour. Phys., 26, 79, (1952); and Nicolet, Sci. Report No. 52, The Pennsylvania State College, Ionosphere Research, (1953)]:

$$N + N \xrightarrow{K} N_2 + h\nu \qquad (e)$$

$$N + O + M \xrightarrow{k_1} NO + M \qquad (f)$$

$$N + N + M \xrightarrow{k_2} N_2 + M \qquad (g)$$

$$N + NO \xrightarrow{k_3} N_2 + O \qquad (h)$$

The relative importance of these various processes are examined and discussed. Two cases are considered with reference to the distribution of atomic nitrogen in the upper atmosphere: the idealistic case of photochemical equilibrium and the non-equilibrium distribution of atomic nitrogen.

In the case of photochemical equilibrium the distribution of atomic nitrogen will be given by

$$n(N) = \sqrt{\frac{J\ n(N_2)}{K}} \qquad (i)$$

where J and K are rate coefficients. J is a function of height as given in the following expression.

$$J = J_\alpha \exp(-\Sigma_k A_k \lambda_1 n_k H_k \sec X)$$

$$J_\alpha = A(N_2) Q_\alpha$$

The value of $\sqrt{\frac{J}{K}}$ lies between 5×10^4 and 5×10^5 depending on the value of Kand Q_α : A table is included which shows the variations of J with height for three different models.

The case of the idealized distribution has only a limited use since it is concerned with a static atmosphere. Under dynamic conditions where the distribution of atomic nitrogen will be governed by mixing and/or diffusion, the following expression is given

$$T_{eq} = \frac{1}{2\sqrt{J K n(N_2)}}$$

where T_{eq} is the time required for $n_t(N)$ to grow to a value of $\frac{e-1}{e} n_{eq}(N)$. The values of T_{eq} were computed for various heights and are included in Table 3 in the report. From this table it may be seen that for photochemical equilibrium to be reached, a period of several years would be required.

The author states that below 150 km where the mixing effect still predominates, the concentration of atomic nitrogen will follow the main atmosphere. From examination of the various rate coefficients the ratio $n(N) / n(N_2)$ may have a value of 1/1000. For the region of transition from mixing to diffusive separation between 150 to 200 km the ratio $n(N)/n(N_2)$ increases to a value of 1/10 at 200 km, while above 200 km atomic nitrogen is distributed according to its own scale height. The concentration of atomic nitrogen need not be larger than $1/10\ n(N_2)$ in order that atomic nitrogen should give adequate ionization

for the F_1 layer. The author points out that such a ratio is not impossible, and that atomic nitrogen will contribute partly to the ionization of the F_1 region. The case of atomic oxygen and its contribution to ionizations in the F_1 and F_2 layers is also briefly discussed.

Mitra, S. K., "Active Nitrogen", Phys. Rev., 90, 516, (1953).

In this paper Mitra has re-examined the older theories of active nitrogen in the well-known nitrogen afterglow. Briefly, the author considers active nitrogen to be a mixture of nitrogen atoms in the ground state ^4S and the metastable states ^2D and ^2P (the latter being in small proportion). The atomic nitrogen is formed by dissociative recombination of N_2^+ ions and electrons which are always present in the strong electric discharge of nitrogen.

The N_2^+ ions and electrons are considered the parent bodies of the active nitrogen instead of themselves being the active substance. The following theories of active nitrogen are discussed. (1) The Ionic Theory.

$$N_2^+ + e^- + M \rightarrow N_2^{(excited)} + M^{(excited)}$$

(2) The Older Theories.

(a) Rayleigh's (1911) theory.

(b) Sponer's (1925) theory.

$$N + N + M \rightarrow N_2^{(excited)} + M^{(excited)}$$

(c) Theory of Cario and Kaplan (1929). The active substance in afterglow is a mixture of metastable molecules in the A state and metastable atoms in the ^2P and ^1D states.

(d) Speculative theories of Birge (1924), Debeau (1942), and Van der Ziel (1934) and (1937).

(3) Metastable Atom Theory.

$$N_2^+ + e^- \rightarrow N^{(excited)}\ (^2D) + N^{(excited)}\ (^2P)$$

(a) Mitra's theory. The active substance in the nitrogen afterglow is a mixture of nitrogen atoms: ^4S (ground state), ^2D and ^2P (metastable states, the ^2P present in only small proportion).

The following topics are considered in the discussion part of the paper: wall effect and long life; chemical activity; spectroscopic excitation; ionization; negative temperature coefficient; and dark modification.

Nicholls, R. W., "The Spectrum of an Argon-Nitrogen Mixture Excited in an High Voltage Arc", J. Chem. Phys., 21, 568, (1953).

The unusual spectrum described in this letter to the editor was interpreted as indicating that the molecules initially excited to low vibrational levels of the a $^1\pi_g$ state (of long lifetime) will populate the adjacent low vibrational levels of B $^3\pi_g$ when secondary collisions with slow electrons occur

Another assumption is that some of the levels of the metastable a' $^1\Sigma_u^-$ and w states are adjacent to the C $^3\pi_u$ levels. The observed spectrum showed only those bands of the 2nd positive system which originate on the v' = O, 1 levels which was considered to be evidence of an indirect excitation mechanism.

Nicolet, Marcel, "Aeronomical Problem of Nitrogen Oxides", Scientific Report No. 52, Ionospheric Research Laboratory, The Pennsylvania State College, 25 October 1953.

With reference to the dissociation of nitrogen molecules Nicolet considers the studies of Bates (1952). Bates used the predissociation found by Herzberg and Herzberg (1948) in the bands of the Lyman-Birge-Hopfield system. The value of the dissociation rate coefficient gave a value $J_{N_2} = 10^{-12}$ sec^{-1} at zero optical depth. A. P. Mitra (1953)

found that the rate coefficient decreases rapidly down with the height in the mesosphere.

Nicolet considers another process which is operative in the ionosphere. Molecular nitrogen is ionized by ultraviolet radiation of $\lambda < 796$ A. The ionization of m lecular nitrogen is followed by dissociative recombination [Bates and Massey (1947)] and is a source of atomic nitrogen. According to Nicolet and Mange (1952 and 1954) diffusion is effective above 160 km and mixing is still active in the E region on the vertical distribution of molecular oxygen. This process exists for atomic nitrogen after its production. The author gives a downward diffusion velocity at 160 km of $1 m\text{-}sec^{-1}$. The author states that the time of diffusion is less than one hour above 200 km and is less than one day above 140 km, while at 100 km the time is more than one month. In addition there are mixing effects. The yield of nitrogen atoms versus height is also dependent upon X-ray action. The downward transport of nitrogen atoms following an ultraviolet ionization process, according to Nicolet, modifies the vertical distribution of atomic nitrogen concentration computed on the basis of a photoequilibrium in a static atmosphere.

Oldenberg, O., "Active Nitrogen, Airglow", Phys. Rev., 90, 727, (1953).

The work reported in this paper was connected with experimental research supported by the U. S. Office of Naval Research. The discussion in the paper includes the following topics: a. theory of the Lewis-Rayleigh afterglow; b. theory of excitation of active nitrogen by Cario and Stille [Z. Phys., 102, 326, (1936)]; c. energy content; d. Kaplan's auroral afterglow; and e. the airglow.

Oldenberg in the present paper gives a modified Cario and Kaplan theory. The author assumes that the recombination of two atoms in a three-body collision makes the energy 9.76 ev available. Resonance

is not effective in this process. As a result excitation of atoms or molecules to any energy below 9.76 ev will occur. The metastable states of atoms and molecules are considered to be important in producing the afterglow.

It is also assumed that a metastable atom with an energy of 2.383 or 3.574 ev transfers its energy to a metastable molecule (in the A $^3\Sigma_u^+$ level) with an energy of 6.21 ev. The results of the author's theory are applied to the night airglow.

Petrie, W. and R. Small, "The Intensities of Atomic and Molecular Features in the Auroral Spectrum", Can. J. Phys., 31, 911, (1953).

This is an extensive report of the careful analysis with a recording microphotometer of a number of auroral spectrograms. The majority of the spectra were from arc and band displays, and the radiation originates mostly near the 100-km level. Integrated intensities were obtained for the main auroral features. The method of calculation of the intensities of atomic features is fully described.

The authors have analyzed a considerable number of moderate dispersion spectra of the aurora. The intensity of the spectral lines are determined from the following relationship:

$$I = N_n A_{nn'} h\nu_{nn'} = N_o \frac{\omega_m}{w_o} e^{-Em/kt} A_{nn'} h\nu_{nn'}$$

where N_n = number of atoms in the upper level involved in the transition,

N_o = number of atoms in the ground level of the atom,

ω_m = the statistical weight of level $_n$,

ω_o = the statistical weight of the ground level,

E_n = the excitation potential of level $_n$, and

T = the temperature of the source.

In addition to O I and O II, N I and N II transitions are discussed. Table III in the paper gives N I intensities and includes ten transitions, their corresponding wavelengths, and excitation potentials. It is stated that atomic nitrogen lines may be produced during collisions with the molecule. Investigations in progress at the Queen's University of Belfast seem to support this conclusion (private communication from D. R. Bates). It is also suggested that a nitrogen molecule dissociates into a neutral and an ionized nitrogen atom, rather that two neutral nitrogen atoms.

$$N_2 + e^- \longrightarrow N + N^+ + 2e^-$$

As a result neutral and ionized atomic lines may be produced in a collision with the molecule. It is considered almost certain that nitrogen atoms are constituents of the normal night atmosphere and that atomic lines will be produced during collisions of these particles.

Nitrogen bands in the auroral spectrum including the negative group bands, second positive group bands, and first positive group bands are also discussed in the paper. A bibliography of 14 references is included.

Reinecke, Ludolf Heinrich, "The Mechanism of the Lewis-Rayleigh Afterglow of Active Nitrogen", Z. Phys., 135, 361-375, (1953).

The first part of this paper is a theoretical discussion and evaluation of current theories of the Lewis-Rayleigh afterglow of active nitrogen. The theory is based upon the value of 9.76 ev for the energy of dissociation of molecular nitrogen. The afterglow is interpreted according to a mechanism involving a three-body collision in which the nitrogen atoms recombine to form molecular nitrogen, either N_2 molecules or foreign gas molecules serving as third bodies.

The second part of the paper describes extensive experiments which the author conducted to investigate the dependence of the afterglow on wall temperatures and foreign gases. The experimental results were interpreted to support the correctness of the proposed mechanisms.

A potential energy showing various molecular states of molecular nitrogen and a photograph of the spectrum of the active nitrogen afterglow are included in the paper.

Sato, Teruo, "On Distribution of Nitrogen in the Upper Atmosphere", J. Geomag. Geoelectr., 5, No. 3, 71, (1953).

This is an excellent paper on the dissociation of nitrogen in the upper atmosphere. The two main mechanisms of the dissociation of molecular nitrogen are considered. The first is the dissociative recombination process elaborated by Bates and Massel [Proc. Roy. Soc. (London), A 187, 261, (1946)]; by Bates [Ann. geophys., 8, 194, (1952); and by S. K. Mitra [Nature, 167, 897, (1951)]. According to this mechanism molecular nitrogen is ionized by radiation of wavelength below λ 795 A. The positive ion thus formed combines with an electron and then dissociates into two nitrogen atoms.

$$\left.\begin{array}{l} N_2 + h\nu \longrightarrow N_2^+ + e^- \\ N_2^+ + e^- \longrightarrow 2N \end{array}\right\} \qquad (a)$$

The second mechanism is that of predissociation suggested by Herzberg and Herzberg [Nature, 161, 283, (1948)]. The nitrogen molecule is excited by radiation between the wavelengths 1150 - 1250 A and later dissociates into two atoms.

$$\left.\begin{array}{l} N_2(X\ {}^1\Sigma_g^+) + h\nu \longrightarrow N_2(a\ {}^1\Pi_g) \\ N_2(a\ {}^1\Pi_g) \longrightarrow 2N \end{array}\right\} \qquad (b)$$

The author also considers the topic of absorption of solar radiation and gives values for the absorption coefficients of both atomic oxygen and atomic nitrogen. Equations are derived for the concentration of ionized nitrogen molecules and for atomic nitrogen. Formulas for the equilibrium are also derived, and calculations are given for the dissociation of molecular nitrogen. Equations are obtained for both the region of small and of large dissociation. In Table 1 the values for $[N_2]/Q$, $[N]$, $[N_2]$, Q, $\int_h^{\infty} Q dh$, and p (for $H_N = 2 \times 10^6$ cm) are tabulated in which the brackets denote the concentration in particles per cm^3, $Q \equiv [N_2] + [N]$, H_N is the scale height, and p is pressure. Distribution curves are included for $[N_2]$, $[N]$, and $[Q]$.

The maximum value of $[N]$ occurs at about 140 - 150 km. The dissociation of N_2 begins at about 130 km and proceeds to completion at about 150 - 160, 160 - 180, and 200 - 220 km corresponding to $k_1 = 10^{-20}$ cm^3/sec, 10^{-19} cm^3/sec, and 10^{-18} cm^3/sec, respectively, in which k_1 is the rate constant of a two-body collision. Two cases were considered, the first in which mechanism (a) and recombination by two-body collision is effective, and the second in which mechanism (b) and a three-body collision is effective.

The author concludes that according to his mathematical deductions dissociation of nitrogen begins at the level of 120 - 130 km and proceeds to completion at about 180 to 220 km. Although the results are not yet conclusive it would appear that nitrogen above the level of about 200 km appears to be almost entirely in the atomic state. Appendix I and Appendix II at the end of the paper are valuable. An excellent list of 17 references is included in the bibliography.

Tanaka, Yoshio, "Extension of the N_2^+ (C → X) Bands in the Far Ultraviolet Region", J. Chem. Phys., 21, 1402, (1953).

In this letter to the editor Tanaka reports the reinvestigation of the N_2^+ (C → X) bands in the far ultraviolet region. An 84-cm normal-incidence vacuum spectrograph was used. It was found that in the case of an uncondensed discharge of pure N_2 and pure NO, no N_2^+ (C → X) bands could be obtained. In the condensed discharge of the pure gases the bands appeared very weakly in the range $v' < 3$.

In the case of the mixture of the gases N_2 with He and NO with He the system of bands appeared strongly in both the condensed and uncondensed discharges. A brief discussion is given of the observations and how they support the theory of predissociation at the $v' = 3$ level.

Versteeg, J. and C. A. Winkler, "The Reaction of Active Nitrogen with Ethylene", Can. J. Chem., 31, 1-3, (1953).

Reference is made to the previous investigation of the reaction of active nitrogen with ethylene at McGill University. Because of the uncertain quantitative results the present investigation was undertaken.

The results of the present investigation are summarized in Figure 1 of the paper. The production hydrogen cyanide

$$C_2H_4 + N \rightarrow HCN + CH_3$$

seemed to confirm the main features of the reaction observed in the previous study. The other curves shown in Figure 1 represent new information.

Of particular interest is the formation cyanogen. The following mechanism is given to explain the reaction:

$$C_2H_4 + N \rightarrow [C_2H_4N]^*$$

$$[C_2H_4N]^* + N \rightarrow [C_2H_4N_2]^*$$

$$[C_2H_4N_2]^* \rightarrow C_2N_2 + 2\,H_2$$

Wainfan, N., W. C. Walker, and G. L. Weissler, "Preliminary Results on Photoelectric Yields in O_2 and N_2 in the Vacuum Ultraviolet", J. Applied Phys., 24, 1318, (1953).

The authors report the absolute photoelectric yields of Pt and Ta and photoionization yields in O_2 and N_2 in the spectral region $\lambda\lambda$ 436-1004 A. In the case of nitrogen (N_2) Figure 5 in the paper shows the photoionization taken at a pressure of 100 microns. The number of ions appearing per 100 photons absorbed is shown to rise rapidly from zero at 796 A (the first ionization limit of N_2) to about 95 at 725 A. The absorption mechanism below 725 A was thought to be due to photoionization, as in the case for O_2.

Winkler, C. A. and H. I. Schiff, "Reactions with Active Nitrogen", Discussions Faraday Soc., 14, 63-70, (1953).

This paper was presented at the meeting for a general discussion on the reactivity of free radicals held 8-9 September 1952 at the University of Toronto. The meeting was sponsored by the Council of the Faraday Society, The National Research Council of Canada, the Chemical Institute of Canada, and numerous industrial companies.

The authors state that they attribute the chemical reactivity of the yellow afterglow to atomic nitrogen rather than to metastable molecules. The present paper is concerned with reactions of active nitrogen with various hydrocarbons. Those considered are methane, ethane, propane, ethylene, and propylene. This research work was supported by

the Defence Research Board, Ottawa, Canada.

The questions during the general discussion period were concerned about the presence of atomic nitrogen as the sole active constituent in the active nitrogen afterglow. Other possible active reactants which were discussed were N_3^* radicals formed by $N_2 + N \rightarrow N_3^*$, metastable molecules, and atomic nitrogen.

1954

Bates, D. R., "The Composition of the Upper Atmosphere. The Problem of Nitrogen", The Observatory, <u>74</u>, 149, (1954).

This is a brief summary f the talk given by Pates at a geophysical discussion on the composition of the upper atmosphere. The meeting was held in the rooms of the Royal Astronomical Society on 26 February 1954. Bates showed a series of diagrams giving the calculated distribution of the allotropes, O, O_2, and O_3 up to an altitude of over 100 km.

With reference to atomic nitrogen Bates stated that nitrogen atoms are produced in the upper atmosphere mainly by dissociative recombination

$$\left.\begin{array}{ll} N_2 + h\nu \longrightarrow N_2^+ + e^- & \text{(a)} \\ N_2^+ + e^- \longrightarrow 2N & \text{(b)} \end{array}\right\}$$

or by predissociation.

$$\left.\begin{array}{ll} N_2 + h\nu \longrightarrow N'_2 & \text{(c)} \\ N'_2 \longrightarrow 2N & \text{(d)} \end{array}\right\}$$

The yield is small in both of the above mechanism. Several secondary processes were considered. Radiative recombination between normal nitrogen atoms

$$2N \rightarrow N_2 + h\nu \qquad \text{(e)}$$

was considered negligible except perhaps at extreme altitudes because it involves a forbidden transition. The direct three-body recombination

$$N + N + M \longrightarrow N_2 + M \tag{f}$$

was considered less effective than the sequence

$$\left.\begin{array}{l} N + O + M \longrightarrow NO + M \\ NO + N \longrightarrow N_2 + O \end{array}\right\} \tag{g}$$

owing both to the relative abundances of the reactants and to the fact that two-body processes are favored at low gas densities.

Mechanism (g) together with the predissociation

$$\left.\begin{array}{l} NO + h\nu \longrightarrow NO' \\ NO' \longrightarrow N + O \end{array}\right\} \tag{h}$$

might dominate well above 100 km. Below 100 km the following reactions were suggested. Nitric oxide might be formed by

$$\left.\begin{array}{l} N + O_2 \longrightarrow NO + O \\ N + O_3 \longrightarrow NO + O_2 \end{array}\right\} \tag{i}$$

or through formation of nitrogen dioxide

$$\left.\begin{array}{l} N + O_2 + M \longrightarrow NO_2 + M \\ N + O_3 \longrightarrow NO_2 + O \end{array}\right\} \tag{j}$$

followed by

$$\left.\begin{array}{l} NO_2 + h\nu \longrightarrow NO + O \\ NO_2 + O \longrightarrow NO + O_2 \\ NO_2 + N \longrightarrow 2NO \end{array}\right\} \tag{k}$$

Nitric oxide may be oxidized by

$$\begin{aligned} NO + O + M &\longrightarrow NO_2 + M \\ NO + O_3 &\longrightarrow NO_2 + O_2 \end{aligned} \qquad (1)$$

Since little is known about the association rates and many of the basic processes are slow, there are many uncertainties and difficulties for quantitative calculations.

Branscomb, L. M., R. J. Shalek, and T. W. Bonner, "Intensity Distributions in Nitrogen Bands excited in Auroras and by High Energy Protons and Hydrogen Atoms", Trans. Am. Geophys. Union, 35, 107, (1954).

The authors state that the primary source of energy for auroras is generally supposed to be a beam of charged particles emanating from the sun. The supporting evidence for this theory includes the (a) doppler shifts in the spectrum, (b) the spatial distribution of auroras relative to the earth's magnetic field, and (c) the reproducible time delay that exists between the appearance of an intense solar flare and the onset of magnetic storms and auroras.

The spectra in this study were obtained by excitation by high-energy protons from the Van de Graaff accelerator of the Rice Institute, Texas. The excitation of vibration in N_2 and N_2^+ bands is included in the discussion. The authors conclude that the 2P bands of N_2 cannot be excited by proton impact, but require electron exchange, electron or neutral atom impact. The 1 N bands of N_2^+ were considered to be more likely excited by proton impact and charge exchange. It is suggested that more than one mechanism is responsible for auroral excitation of nitrogen bands, and that the balance between the mechanisms will vary with time and location.

Broida, H. P. and J. R. Pellam, "Phosphorescence of Atoms and Molecules of Solid Nitrogen at 4.2°K", Phys. Rev., 95, 845-846, (1954).

The authors observed a phosphorescent glow in the solid products from an electrodeless discharge through nitrogen gas at low pressure in attempting to freeze out radicals at liquid helium temperatures. The nitrogen traversed a region at low pressure between 0.1 and 3 mm Hg. The discharge was excited by means of a microwave (2450 Mc/sec) voltage. The apparatus and experimental technique are fully described.

Reference is made to the early work of Vegard and McLennan and Shrum who observed green glow upon bombarding solid nitrogen with cathode and canal rays. The phosphorescence observed by Broida and Pellam was considered to be identical to that observed by Vegard and McLennan.

The observations reported in this paper were considered to constitute evidence for the existence of atoms coexisting with molecules in the solid phase. Similar conclusions were made from the collection of atoms of hydrogen and oxygen and OH radicals from water vapor at temperatures of liquid helium.

Brook, M. and J. Kaplan, "Dissociation Energy of NO and N_2*", Phys. Rev., 96, 1540, (1954).

The authors have reexamined the β bands ($B\ ^2\Pi \rightarrow X\ ^2\Pi$) of NO. The purpose was to establish the dissociation energy of N_2, since the dissociation energy of NO is related to the dissociation of N_2 by the reaction

$$N_2 + O_2 + 1.87\ \text{ev} \rightarrow 2NO .$$

From past spectroscopic studies the dissociation energy for N_2 $[D_o(N_2)]$ has been found to be either 7.37 ev or 9.76 ev; and for the NO molecule $D_o(NO)$ is either 5.29 ev or 6.48 ev.

The experimental procedure was to excite the β bands of NO by introducing a small amount of oxygen into active nitrogen. A quartz discharge tube was employed using a vacuum tube oscillator of 1.5-kw input power. Spectrograms were taken through a quartz window of the afterglow spectrum. From Figure 2 in the paper [a plot of $\Delta G(v)$ vs $G(v)$ for the observed levels of the $X\ ^2\Pi$ ground state of NO] the authors conclude that if $D_o(NO)$ has a value of 5.29 ev a very sharp and sudden drop in the $\Delta G(v)$ values would be necessary. No such tendency was observed, giving reason to believe that the higher value of $D_o(NO)$, 6.48 ev, was most probable. This higher value establishes $D_o(N_2)$ to be 9.76 ev.

Clarke, E. M., "Ionization Probability Curves Using an Electron Selector. Results on N_2^+, N^+, Xe^{++}", Can. J. Phys., 32, 764-774, (1954).

The apparatus employed in this investigation consisted of an electron selector built into a mass spectrometer. The description and arrangement of the instrumentation are described in full. Initial ionization curves were obtained and the interpretation of the curves is discussed. The following new measurements were obtained. From these data it was possible to calculate the energy of dissociation of N_2. In the process

$$N_2(X\ ^1\Sigma_g^+) \longrightarrow N^+(^3P) + N(^4S^0)$$

the following energy relation obtains

$$A_o = D(N_2) + I(N) + E_e(N^+) + E_e(N)$$

where A_o is the appearance potential, D is the dissociation energy, I is the ionization potential, and E_e is the electronic excitation energy. The mean value for A_o taken from several ionization curves is 24.35 ± 0.1.

$$D(N_2) - 24.35 - 14.54 - 0 - 0 = 9.81 \text{ ev.}$$

In the process

$$N_2(X\ ^1\Sigma_g^+) \longrightarrow N^+(^3P) + N^*\ (^2D^0)$$

$A_o = 26.71$ and thus $D(N_2) = 26.71 - 14.54 - 0 - 2.38 = 9.79$ ev. The latter value is in agreement with that reported by Douglas [Can. J. Phys., 30, 302, (1952)].

The following data for nitrogen are summarized: $^2\Pi_u$ state of N_2^+ at 1.0 ± 0.2 ev above initial potential; $^2D^0$ state of N^+ at 2.36 ev above the $^4S^0$ state; and $^2P^0$ state of N^+ at 1.4 ev. above the $^2D^0$ state.

Costello, M., H. Serson, R. Montalbetti, and W. Petrie, "The Occurrence of Ionized Nitrogen Bands in the Twilight Spectrum", Can. J. Phys., 32, 562, (1954).

In this letter to the editor the authors have attempted to determine whether or not N_2^+ ions are present in the undisturbed ionosphere. If these ions do occur they should contribute to the total ionization of the E-layer. Also the presence of N_2^+ ions are present in the atmosphere.

The twilight spectrum was photographed in the region of the (0,0) N_2^+ bands at 3914 A with a plane-grating spectrograph of 40 A/mm. Thirty-five satisfactory plates were obtained at Ottawa and fifty-seven at Rosolute Bay. An examination of the spectra and magnetic data revealed that the 3914 A band of N_2^+ was observed only when magnetic disturbances occurred. If the 3914 A band is not in the twilight spectrum during magnetically quiet periods, this was interpreted to mean that

either there are very few N_2^+ ions present in the normal atmosphere, or else they are removed very rapidly by some process so that the number of quanta radiated in the 3914 A band is small.

Curtis, J. P., "Absorption Coefficients of Air and Nitrogen for the Extreme Ultraviolet", Phys. Rev., 94, 908, (1954).

In this paper the author describes a method to study absorption of air and nitrogen in the extreme ultraviolet. Absorption coefficients for dry air and nitrogen were measured in the spectral region 150 -1000 A. The values are given in Table 1 of the paper. The method employed, instrumentation, and technique are described.

Dufay, Maurice, "The Spectrum of the Night Sky from 3380 to 4200 A", Compte, rend., 239, 533-536, (1954).

The observation of the band at 3913 A which the author attributed to the (0,0) transition of N_2^+ is reported in the present paper. The band was strengthened when the N_2^+ bands appeared with intensity during the preceding twilight.

Faire, A. C., O. T. Fundingsland, and A. L. Aden, "Measurement of Dissociative Recombination in Nitrogen", Phys. Rev., 93, 650, (1954).

This is an abstract of a paper presented at the sixth annual conference on gaseous electronics held at Washington, D. C., 22-24 October 1953.

The authors report their laboratory investigations of recombination of thermal electrons with molecular ions in nitrogen using a microwave method. Helium was added to the molecular nitrogen in proportions such as to maintain a total gas pressure high enough to subordinate ambipolar diffusion to the walls of a microwave cavity.

The value of the recombination coefficient obtained from the measurements was of the order of 10^{-6} cm^3/sec^{-1}.

Fan, C. Y., "The Possible Role of Accelerated Secondary Electrons in Aurora", Astrophys. J., 119, 294, (1954).

In this note to the Astrophysical Journal the author describes laboratory experiments made at Yerkes Observatory on the interaction of high energy ions with air. Protons and He^+ energies ranging in steps from 40 to 400 kev and air pressure of about 10^{-1} mm Hg were employed. A new series of experiments is reported using electrons ranging from 0.2 to 7 kev. It was found that the electrons were the only particles able to excite the Meinel N_2^+ system efficiently.

Three possible conclusions are discussed for the excitation of the Meinel bands. The author suggests that the electrons are of secondary origin. It was thought unlikely that the energetic secondary electrons are the result of ionizations. It is concluded that the secondary electrons must subsequently have been accelerated to energies of several hundred volts which would require the presence of a potential gradient in the auroral regions.

Fan, C. Y., "Excitation of Air Glow by Electronic Impact", Phys. Rev., 96, 860, (1954).

This is an abstract of a paper read before the Pacific Northwest meeting of the American Physical Society held at the University of Washington, 7-10 July 1954. The author discusses his spectrographic study of the optical emission from rarefied air samples under the bombardment of an electron beam of energy from 10 to 8000 ev. The spectral range was 3800 to 9000 A. The spectra are quite different from those excited by protons or heavier ions. The Meinel system for N_2^+ and the first negative system of O_2^+ are distinctive in the spectra excited by electronic impact but are practically missing from spectra excited by protons. This observations has an application to the excitation mechanism

of the aurora borealis.

Harteck, P. and S. Dondes, "The Decomposition of Nitrogen Dioxide by Neutraon Irradiation", J. Chem. Phys., 22, 953-954, (1954).

The authors give the following reaction mechanism of nitrogen dioxide when illuminated with ultraviolet light.

$$NO_2 + h\nu = NO + O \qquad (a)$$

$$NO_2 + O = NO + O_2 \qquad (b)$$

$$2\,NO + O_2 = 2\,NO_2 \qquad (c)$$

Nitrogen dioxide is primarily dissociated by ionizing radiation according to

$$NO_2 + h\nu = N + O + O \qquad (d)$$

The question is considered whether nitrogen atoms react only according to the reaction

$$NO_2 + N = 2\,NO \qquad (e)$$

The NO_2 which decomposed according to reaction (d) was found not to react completely according to reaction (e). By experiment the following products were found: nitrogen dioxide, almost equal quantities of nitrogen and oxygen, and nitrous oxide. To account for these reaction products the following reactions seemed probable:

$$NO_2 + N = N_2O + O + 43\text{ kcal} \qquad (f)$$

$$N_2O + h\nu = N_2 + O \qquad (g)$$

$$NO_2 + N = N_2 + 2\,O + 3.5\text{ kcal} \qquad (h1)$$

$$\text{and} \quad N_2 + O_2 + 120.7\text{ kcal} \qquad (h2)$$

Heald, Mark A. and Robert Beringer, "Hyperfine Structure of Nitrogen", Phys. Rev., 96, 645-648, (1954).

The magnetic resonance spectrum of the ^4S ground state of atomic nitrogen-14 was observed using the microwave method. The ground electronic configuration of the nitrogen atom is $2p^3$ which forms the Russell-Saunders terms ^4S, ^2D, and ^2P. The $^4S_{3/2}$ state is the normal ground state the N^{14} nucleus possesses both magnetic dipole and electric-quadruple moments.

The authors state that the production of atomic nitrogen is intimately connected with the phenomenon of "active nitrogen". A brief review is given of previous investigations on active nitrogen. In the present investigation a condensed discharge was employed to obtain nitrogen atoms in the ground ^4S state. A high voltage power supply charged a 5-μf capacitor through a 20,000-ohm resistor. A long U-shaped tube with aluminum electrodes was connected in parallel with the capacitor; discharge occurred about eight times per second.

No trace of the magnetic resonance spectra from the metastable ^2D and ^2P states was observed. A three-line spectrum arising from the $^4S_{3/2}$ ground state of the N^{14} atom was observed. The lines appeared of equal intensity and width and were equally spaced. The magnetic dipole hyperfine interaction constant is

$$A = 10.45 \pm 0.02 \text{ Mc/sec.}$$

No evidence was obtained for electric quadrupole interaction.

Hendrie, J. M., "Dissociation Energy of N_2", J. Chem. Phys., 22, 1563, (1954).

The research reported in this paper is an attempt to determine the dissociation energy of molecular nitrogen, $D(N_2)$. Literature references are given for this controversial subject. Most investigators prior to 1951

preferred the value 7.385, ev; however recent experiments give strong support to the value 9.765 ev. The purpose of the work reported by Hendrie is to choose between the values 7.385 ev and 9.765 ev for $D(N_2)$ by observations at high temperatures and low pressures.

The apparatus employed is described in detail. The highest temperature of the oven from which the observations were made was $3530^{\circ}K$. The procedure used in the runs is described and calculations for fractional dissociation in the oven are given. The theoretical dissociation is discussed through use of the usual equilibrium equations involving (a) the equilibrium constant, (b) the total and partial pressures,

$$N_2 \rightleftharpoons 2N$$

(c) the fractional dissociation, and (d) free energy of the components.

The author concludes from his results that the dissociation energy of N_2 is presumably 9.765 ev without any ambiguity, thus eliminating the lower value, 7.385 ev. The results do not confirm the higher value 9.765 ev but it is emphasized that they set a lower limit to $D(N_2)$ at 8.80 ev.

Johnston, W. H. and R. M. Anstett, "The Homomolecular Exchange of Nitrogen in a Glow Discharge", J. Chem. Phys., 22, 146, (1954).

In these experiments with glow discharge a mass spectrometer was employed to follow the approach of isotopic equilibrium in a mixture of N_2^{28}, N_2^{29}, and N_2^{30} molecules containing fifteen percent nitrogen-15. Table I in the paper gives the actual rates of exchange and effective electron yields. Reference is made to Mitra's [phys. Rev., 90, 516, (1953)] dissociative recombination of N_2^+ ions and electrons theory. The authors suggest that if this process is responsible for the majority of the charge transfer at the cathode, it follows that recombination of the

nitrogen atoms on the metal electrodes or walls would produce exchange with an "effective electron yield" of unity. An atomic chain reaction $N + N_2$ could reasonably be expected to have an "effective electron yield" from 0 to 10^{+6} and would depend upon the rate of the chain-breaking reaction and the rate of exchange. The atom-recombination mechanism of exchange is favored because of the improbability of finding a yield of unity in the experimental value.

Kaplan, Joseph, "Laboratory Studies Related to the Physics of the Upper Atmosphere", I.U.G.G. Assoc. Terrest. Mag. Elect., I A T M E Bull., 14, 249-254, (1954).

This is a paper read before the 21 Autust - 1 September 1951 meeting at Brussels. The report is concerned chiefly with the oxygen system. The following reactions are included as possible sources of NO_2, NO, and N in both the laboratory and the atmosphere.

$$N_2 + O_3 \rightarrow NO + O_2$$

$$NO + O(^1D_2) \rightarrow N(^4S) + O_2 \quad [^1\Sigma(v' = o)]$$

$$NO + O(^1S_O) \rightarrow N(^2D) + O_2 \quad [^1\Sigma(v' = o)]$$

The following reaction is suggested to account for the excitation of the Vegard-Kaplan bands in the night airglow.

$$N(^4S) + N(^2D) + M \rightarrow N_2 (A\ ^3\Sigma) + M$$

Mitra, A. P., "A Tentative Model of the Equilibrium Height Distribution of Nitric Oxide in the High Atmosphere and the Resulting D-Layer", J. Atm. Terrestr. Phys., 5, 28, (1954).

This paper is a condensed treatment of the author's Scientific Report No. 46, Ionospheric Research Laboratory, The Pennsylvania State College, 15 May 1953 under the same title. For the summary of the

present paper see that for Scientific Report No. 46, p. 359 in this volume, where the portion pertaining to atomic nitrogen in the upper atmosphere is summarized.

Mitra, A. P., "Atomic Nitrogen as a Constituent for Region F_1", Indian J. Phys., 28, 269, (1954).

The purpose of this paper is to consider the case of atomic nitrogen as an active constituent of the F_1 Region. The atmospheric constituents present in sufficient number are considered to be atomic oxygen, molecular nitrogen, and possibly atomic nitrogen. The author states that atomic oxygen, at the first ionization potential, gives an ionization maximum in a location somewhere between the E and F_1 regions; and that the evidence of twilight spectra precludes the possibility of N_2^+ [Bates, Proc. Roc. Soc. (London), A 196, 562, (1949)].

Because of the general belief that the dissociation efficiency of N_2 is very low outside the auroral region and becuase of the absence of a simple photodissociation process for N_2 dissociation analogous to that of O_2, and in addition the presence of molecular nitrogen at high altitudes in sunlit auroras, have contributed to overlooking the possible ionization of atomic nitrogen as a process in the ionosphere. These objections have largely been removed at the present time due to the discovery of atomic nitrogen lines in the spectrum of the airglow by Courtes (1950) and Dufay (1951), and also to the production of atomic nitrogen by a dissociation recombination process suggested by Bates (1952) and S. K. Mitra (1951). At high altitudes the following reactions may occur.

$$N_2 + h\nu \xrightarrow{\lambda < 795\ A} N_2^+ (X') + e^- \qquad \text{(a)}$$

$$N_2^+ (X') + e^- \longrightarrow N(^2P) + N(^2D)$$

and at lower heights atomic nitrogen may be formed by the Herzberg-Herzberg process (1948),

$$N_2 + h\nu \xrightarrow{\lambda\lambda 1150-1250\ A} N_2\ (a\ {}^1\Pi_g) \qquad \text{(b)}$$

$$N_2\ (A\ {}^1\Pi_g) \longrightarrow N + N$$

Nicolet and Pastiels (1952) and Nicolet (1950) have suggested that N_2 may be produced by

$$N + N^+ \longrightarrow N_2^+ \qquad \text{(c)}$$

The author states that in the F_1 region (150 to 250 km) most of the atmosphere is in diffusive equilibrium; however at lower levels of about 150 km there is probably a transitional state between mixing and diffusion. Beginning with the theory of Chapman the author derives equations for the rate of electron production, the height of maximum ionization, and the distribution of atomic nitrogen in the upper atmosphere. In the case of atomic nitrogen both the distribution of atomic nitrogen and atomic nitrogen as a constituent of the F_1 region are considered. Atomic nitrogen is produced by either of processes (a) or (b) above. In the case of the F_1 region mechanism (a) need only be considered. The following processes account for the disappearance of nitrogen atoms.

$$N + N \xrightarrow{K} N_2 + h\nu \qquad \text{(d)}$$

$$N + O + M \xrightarrow{k_1} NO + M \qquad \text{(e)}$$

$$N + N + M \xrightarrow{k_2} N_2 + M \qquad \text{(f)}$$

$$N + NO \xrightarrow{k_3} N_2 + O \qquad \text{(g)}$$

The author states that below 150 km where the mixing effect predominates, the concentration of atomic nitrogen will follow the main atmosphere. The value of the ratio $n(N)/n(N_2) = 1/100$ is considered a reasonable estimate. The ratio $n(N)/n(N_2)$ increases to a value of 1/10 at 200 km. In order that atomic nitrogen may give adequate ionization in the F_1 region Mitra considers that the concentration of atomic nitrogen need not be greater than $1/10\ n(N_2)$ at a height where diffusive separation occurs. Above 200 km it is concluded that atomic nitrogen is distributed according to its own scale height.

Nicholls, R. W., "High-Voltage Arcs in Argon-Nitrogen Mixtures", Nature, 173, 495-496, (1954).

Probable excitation mechanisms involving vibrational levels of the X $^1\Sigma_g^+$ state of N_2 are discussed. This explanation now appears to be superior to the mechanism previously proposed by the author [J. Chem. Phys., 21, 568, (1953)]. It is considered that the energy exchanges involve atoms and molecules in metastable states. From recently computed values of vibrational transition probabilities of the Lyman-Birge-Hopfield system it appears that levels v = 2, 3, 4, 5, of the X $^1\Sigma_g^+$ state will be preferentially populated.

Nicolet, M., "Dynamic Effects in the High Atmosphere", The Earth as a Planet, edited by G. P. Kuiper, The Solar System, Vol. II, Chapter 13, pp. 680-699, University of Chicago Press, (1954).

The topics discussed which pertain to atomic nitrogen in the upper atmosphere are (a) decomposition of nitrogen, (b) nitrogen recombination, (c) ratio of concentration of atomic to molecular nitrogen, (d) the Airglow and Atomic Nitrogen, and (e) several topics on nitrogen oxides in the upper atmosphere. Atomic nitrogen is involved in the formation and decomposition of many of these oxides of nitrogen.

With regard to the decomposition of molecular nitrogen reference is made to the theoretical photochemical studies by Bates. The value of the dissociation rate coefficient is $J_{N_2} = 10^{-12}$ sec^{-1} according to the Herzberg predissociation mechanism at about 1240 A supposed to occur in the mesospheric regions. The ionization dissociation recombination assumed to occur in higher regions of the atmosphere is also discussed. The following data are included. Ionization by radiation of $\lambda < 796$ A and $\lambda < 661$ A,

$$N_2 \xrightarrow{\lambda < 796 \text{ and } \lambda < 661 \text{ A}} N_2^+ + e^-$$

according to Weissler, Lee, and Mohr (1952) the absorption coefficient is 2.2×10^{-17} cm^2. The number of photons available at the top of the earth's atmosphere is given by Nicolet as having a value of 2×10^9 photons cm^{-2} sec^{-1}. The ionization rate coefficient at zero optical depth is about 4.4×10^{-8} sec^{-1}.

For the reaction

$$N_2^+ + e^- \longrightarrow N + N$$

the rate coefficient is about 10^{-6} cm^{-3} sec^{-1} according to Biondi [Phys. Rev., 83, 1078, (1951)]. The lifetime is

$\tau\ (N_2^+) = \frac{1}{an_e}$ < 100 seconds in the F region of the ionosphere.

The value of the height of the maximum rate of atomic nitrogen at X = O is

$R_M^*(N) \geq 8 \times 10^2$ cm^{-3} sec^{-1} at 160 km. Again making reference to the data of Bates the author gives

$$\frac{n(N)}{n(N_2)} \qquad \frac{J_2}{a_o n(M) n(O)}$$

where $a_o = 1.5 \times 10^{-32}$ cm^6 sec^{-1} (the rate recombination coefficient), therefore at 160 kilometers

$$J_2 \geq 2.6 \times 10^{-8} \text{ sec}^{-1}$$

and

$$\frac{n(N)}{n(N_2)} \geq 3.8 \times 10^3$$

In summing up the deductions, the author has included graphs of the rate of atomic nitrogen production, the velocity of diffusion of nitrogen atoms, and the time of diffusion, all plotted, versus altitude.

Seaton, M. J., "Excitation Processes in the Aurora and Airglow. 1. Absolute Intensities, Relative Ultraviolet Intensities, and Electron Densitites in High Latitude Aurorae", J. Atm. Terrestr. Phys., 4, 285, (1954).

With reference to absolute brightness of the aurora the author states that the apparent visual brightness might be expressed in terms of a quantity π_ν (5550), the equivalent number of photons in the wavelength of maximum visual sensitivity. This is equal to 5.6×10^{16} times the surface brightness in candles/cm^2. Since a high proportion of the visual brightness comes from the oxygen green line, λ5577 A, the author states that π (5577) is equal to $1/2\ \pi_\nu$ (5550). Using this relation absolute brightness may be expressed in terms of π (5577).

The author gives the value of electron densities, based on radio and optical evidence, between 10^7 and 10^8 cm^{-3} in high latitude aurorae. From optical evidence the N_2^+ negative group is emitted after simultaneous ionization and excitation of N_2 [Bates, Proc. Roy. Soc. (London), A 196, 217, (1949)].

Seaton, M. J., "Excitation Processes in the Aurorae and Airglow. 2. Excitation of Forbidden Atomic Lines in High Latitude Aurorae", J. Atm. Terrestr. Phys., 4, 295, (1954).

Reference is made to the work of Bernard (1941), Petrie and Small (1952), and Gartlein and Sherman (1952) who have shown that the forbidden lines of N I $\lambda\lambda$3467 and 5199 A are regularly excited in high latitude aurorae. The author states that the relative intensities of the N I lines are much less certain than those of the O I lines. The cause is partly due to the fact that λ5199 is a faint feature and λ3467 is in a region where the ultraviolet correction factor is large. The dissociation recombination mechanism

$$N_2^+ + e^- \longrightarrow N' + N''$$

is considered and the following table is included.

I (3467) due to dissociative recombination

n(e) cm^{-3}	Lower limit for I (3467) [I (5577) = 100]
10^6	62
10^7	50
10^8	18

The author concludes that the N I lines are excited by dissociative recombination of N_2^+. This mechanism seems capable of accounting for the observed intensity I (3467) equal to 120.

$$\frac{I\ (3467)}{I\ (5577)} = \frac{120}{100}$$

Sen Gupta, Prabhat K., "Nature of Active Nitrogen", Sci. and Culture, 19, 414, (1954).

The author states that the natur ˆ active nitrogen in afterglows has not yet been established with certainty. Reference is made to Saha and Sur [Phil. Mag., 48, 21, (1924)]; and to Cario and Kaplan [Nature, 121, 906, (1928)], who ascribed the activity to the presence of metastable nitrogen molecules or atoms or both. The purpose of the present paper is to interpret the main spectroscopic features and to postulate that active nitrogen consists of hihgly excited metastable nitrogen molecules.

Included in the paper is a discussion of Kaplan's (1948) laboratory experiments of afterglows in nitrogen which reproduced the spectra of the aurora and night sky. Kaplan obtained spectra which contained the first negative bands of N_2^+, the Vegard-Kaplan bands, first and second positive bands of N_2, and the forbidden line $\lambda 3467$ ($^2P \rightarrow {}^4S$) of N I. Seven mechanisms are given in the paper and each is briefly discussed.

$$N_2(A) + N_2(X) \longrightarrow N_2(B)_{v'} = 12, 11, 10 \ldots \qquad \text{(a)}$$

8.0 - 9.6 ev

$$N_2(A) + O_2 \longrightarrow O(^3P) + O(^1S) \qquad \text{(b)}$$

9.26 - 9.60 ev

$$N_2^+ (X') + e^- + N_2(X) \longrightarrow N_2(A) + N_2(A) \qquad \text{(c)}$$

15.5 ev 9.44 - 8.00 ev, 6.14 - 7.52 ev

$$N_2(A) + N_2(X) \longrightarrow N_2(B)_{v'} = 11, 10 \ldots + N_2(X) \qquad \text{(d)}$$

8.00 - 9.44 ev 9.43 ev

$$N_2^+(X') + e^- \longrightarrow N(^2P) + N(^2D) \qquad \text{(e)}$$

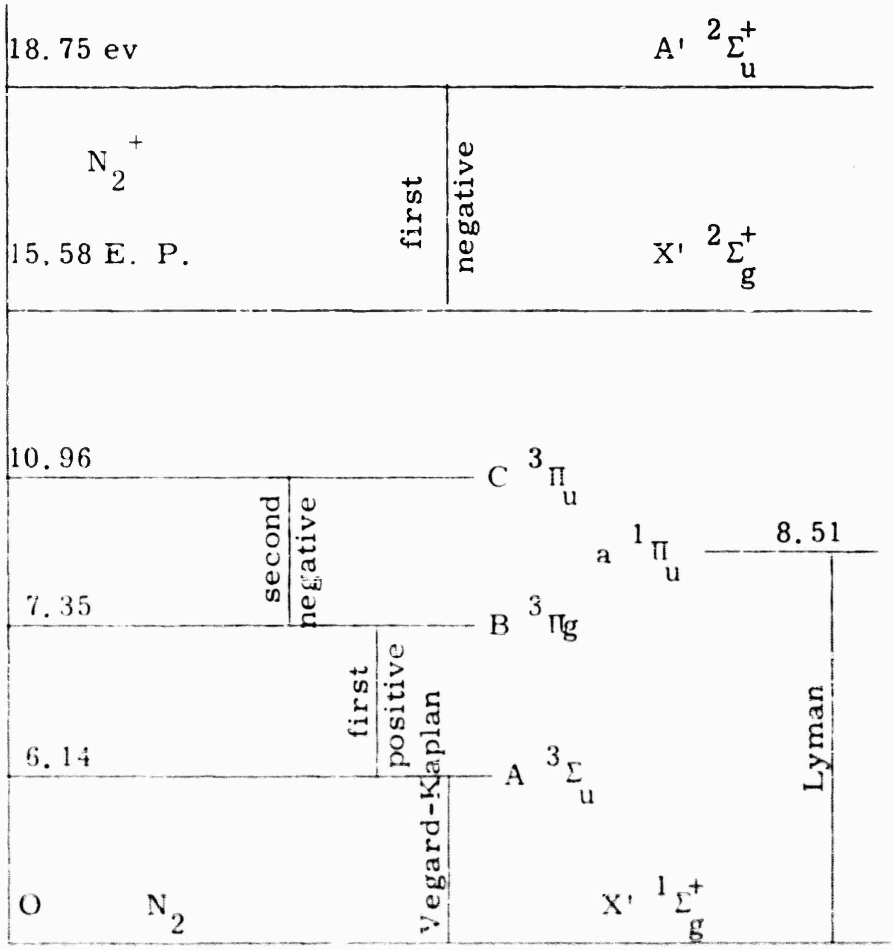
15.58 v K. E. 3.56 2.37 ev

$$N_2(A) + N(^2P) \longrightarrow N_2(C) + N(^4S) \qquad \text{(f)}$$

8.00 - 9.44 ev 3.56 ev

$$N_2^+(X') + N(^2P) \longrightarrow N_2(A') + N(^4S) \qquad \text{(g)}$$

15.58 ev 3.56 ev 19.14 ev



Stanley, C. R., "A New Method for the Production of Active Nitrogen and its Application to the Study of Collision Effects in the Nitrogen Molecular Spectrum", Proc. Phys. Soc., A67, 821-827, (1954).

A high tension capillary arc source for the production of active nitrogen is described. The details are shown in a diagram of the apparatus included in the paper. A brief history of the discovery of an active modifica-

tion of nitrogen is given in the introduction. Other topics considered are the spectrum of the afterglow at low pressures and the spectrum of the afterglow at higher pressures.

In the discussion portion of the paper the author states that the nature of the active nitrogen and its production of the afterglow are still in doubt. The theories of the afterglow of active nitrogen by Mitra (1953), Oldenberg (1953), and Cario and Reinecke (1949) are discussed.

The author states that a change in the intensity distribution throughout a band system implies a change in the distribution of vibrational energy among the molecules in the excited electronic state. It is concluded that the exchange of vibrational energy occurring in collisions between the excited nitrogen molecules and the other molecules present can best explain the results.

The following mechanism is given:

$$N(^4S) + N(^4S) + N_2(v_1) \rightarrow N_2(B^3\Pi_g) + N_2(v_2)$$

where v_1 and v_2 denote the initial and final velocities of the inert molecule.

$$I = C(T)\ n^2\ p$$

The intensity, I, of the afterglow is expressed by the above expression where n is the concentration of active particles, p is the pressure of the inert gas, and C(T) is a parameter depending on the temperature.

Swings, P., "Reflections on a Corpuscular Theory of Emission from the Night Sky", Scientia, 89, 5-12, (1954).

The author considers that certain emissions in the night sky spectrum due to O I, Na, O_2, and N_2 originate at altitudes of about 200 km. According to the theory presented in this paper the emissions results from

collisions of extra-terrestrial particles (protons of energy 10 kv) with the atmospheric constitutents. This results in the production of semi-permanent low-energy auroral discharge.

Tanaka, Yoshio, "Emission Bands of NO in the Vacuum Ultraviolet Region Excited in the NO Afterglow", J. Chem. Phys., 22, 2045-2048, (1954).

Since the dissociation energy of NO is related to the dissociation of N_2, the present study by Tanaka is a valuable contribution to the controversial question about the $D(N_2)$. Spectrograms are shown in Figure 1 in the paper for the emission bands of NO in the NO afterglow and in an ordinary discharge of NO. Potential energy curves of the NO molecule are illustrated in Figure 2.

The following reactions are suggested as occurring to produce the strong NO bands:

$$NO(X\ ^2\Pi) + N(^4S) + O(^3P) \rightarrow NO^* + NO(X\ ^2\Pi) \qquad (a)$$

$$NO^* \rightarrow NO(X\ ^2\Pi) + h\nu \quad (\beta,\ \gamma,\ \text{and } \delta \text{ bands}) \qquad (b)$$

The above observations in the present investigation could be explained without difficulty from the above reactions by accepting the value of $D(NO) = 6.48$ ev.

Another reaction involving atomic nitrogen is

$$N_2(X\ ^1\Sigma_g^+) + N(^4S) + O(^3P) \rightarrow N_2^* + NO\ (X\ ^2\Pi) \qquad (c)$$

The above reaction is expected to occur because the main constituent in the glow should be the N_2 molecule in its ground state. Reference is made to the new theory of Cario and Reinecke (1953) on the mechanism of the Lewis-Rayleigh afterglow of active nitrogen. The theory involves an inverse predissociation of nitrogen atoms along the $^5\Sigma_o$ potential curve arising from dissociation products $N(^4S) + N(^4S)$. The author

concludes that the interpretation of the observed abrupt cut-off at certain v' values in β, γ, and δ bands and the complete non-appearance of ϵ and β' bands favor the value of $D_o(NO) = 6.48$ ev.

Tawde, N. R. and K. S. Korgaonkar, "Relative Roles of Oxygen and Air in the Development of Some Nitrogen Band Systems", Bul. soc. roy. sci., Liege, 23, 435, (1954).

The authors in the present paper have reported their study of the influence of oxygen and argon on N_2 (^1P) and (^2P) systems in discharges through nitrogen. A brief review is given of previous work by various investigators. Tawde and Patankan (1944, 1947) attributed the pink color of discharge through air as compared to the bronze color through pure nitrogen to the formation of active nitrogen under the influence of the rare gases. Gaydon (1944, 1948) studying the same phenomena considered the predominance of the pink color to be the effect on nitrogen of the oxygen content of air. Because of these conflicting views the present investigation was undertaken in a quantitative way by studying the overall intensity distribution in the 1st and 2nd positive systems.

The results of intensity values of all the measurable bands of the N_2 (^1P) and (^2P) systems are tabulated in Table I of the paper. The observations lead to the conclusion that the suppression effect on the (^1P) system rather than on the (^2P) system in air as against that in pure nitrogen is largely due to the oxygen content of air. This in general supported Gaydon's explanation. The several topics included in the discussion are electronic excitation, excitation through metastables, deactivation process, and active nitrogen hypothesis.

1955

Barbier, D. "Analysis of the Night-Sky Spectrum", Ann. geophys., 11, 181-208, (1955).

This is an extensive survey on the topic of analysis of the night-sky spectrum also published in the I.A.G.A. Bulletin, No. 15b, "Problems of the Physics of the High Atmosphere", Communications presented the Rome Reunion, September 1954. The topics considered in this report are:

a. Airglow Spectrographs,

b. References to the Airglow Spectra,

c. The Absorption Spectrum of the Airglow,

d. The Emission Continuous Spectrum,

e. Atomic Lines,

f. OH Rotation - Vibration Bands,

g. Atmospheric System of O_2,

h. Suggestions concerning Various Systems of Molecular Oxygen,

i. Negative Systems of N_2,

j. The Vegard-Kaplan System of N_2,

k. Other Systems,

l. Conclusions.

An extensive bibliography of 74 references is appended which greatly enhances the value of this excellent survey.

Bates, D. R. "Theory of the Auroral Spectrum", Ann. geophys., 11, 253-279, (1955).

This paper is also published in the I.A.G.A. Bullentin, No. 15b, of the I.U.G.G. under the title "Probleimes de la Physique de la Haute Atmosphere", Communications presented at the Reunion at Rome in September 1954 under the auspices of International Association of

Terrestrial Magnetism and Electricity, Paris, (1956). The present paper is a very extensive and comprehensive treatise of the theory of the auroral spectrum.

It is stated that the main luminescence observed is due to a. inelastic collisions made by the incident particles and by the ejected electrons (which may possess kinetic energy other than that given them initially), b. degradation of the ultraviolet radiation emitted and, in the case of sunlit auroras, scattering of solar radiation, c. thermal processes such as dissociative recombination.

With reference to atomic nitrogen there is the possible argumentation of the abundance of atomic nitrogen by impact dissociation and, more especially, by dissociative recombination.

$$N_2^+ \ (X\ ^2\Sigma_g^+) \ + e^- \longrightarrow N' \ + \ N''$$

The rate coefficient for this reaction may be as high as 10^{-6} cm^3 sec^{-1}. In this connection reference is made to the work of Biondi and Brown [Phys. Rev., 76, 1697, (1949)] and Faire, Fundlingsland, and Aden [Phys. Rev., 93, 650, (1954)] .

The following transition probabilities are given for N I:

N I	$^2P \longrightarrow {}^4S$	5.4×10^{-3} sec^{-1}
	$^2P \longrightarrow {}^2D$	2.3×10^{-1} sec^{-1}
	$^2D \longrightarrow {}^4S$	1.0×10^{-5} sec^{-1}

With reference to the forbidden N I lines from the work of Seaton [J. Atmos. Terrestr. Phys., 4, 295, (1954)] the reaction

$$N(^4S) \ + \ e^- \longrightarrow N(^2D \text{ or } ^2P) \ + e^-$$

was shown unable to account for the observed λλ 5199 and 3467 A intensities. The following reactions are given which might seem more effective.

$$N_2(X\ ^1\Sigma_g^+) + X \rightarrow N + N(^2D \text{ or } ^2P) + X$$

$$N_2^+ (X\ ^2\Sigma_g^+) + e^- \rightarrow N + N(^2D \text{ or } ^2P)$$

A list of 81 literature references is given in the appended bibliography.

Bates, D. R. and B. L. Moiseiwitsch, "Energies of Normal and Excited Negative Ions", Proc. Phys. Soc. (London), A68, 540-542, (1955).

Since there are difficulties associated with direct determination, the method of estimating the electron affinities of atoms by extrapolation procedures has been used by a number of investigators. The method of Glockler [Phys. Rev., 46, 111, (1934)] is cited as a procedure yielding useful results. It is assumed that A, the detachment potential of a negative ion, may be obtained from I_o, I_1, and I_2, the ionizing potentials of the neutral atom and singly and doubly charged positive ions of the iso-electronic sequence, by quadratic extrapolation.

$$A = 3I_o - 3I_1 + I_2$$

The case of N^- (^1D) is given special mention. The total energy is estimated to be well below that of $N(^2D)$, the excitation potential of which is 2.38 ev. As a result the only energetically allowed distintegration is

$$N^- (^1D) \rightarrow N(^4S) + e^-$$

which involves a forbidden radiationless transition. The life of N^- (^1D) towards auto-detachment, though still brief, should be less transitory than is usual for unstable negative ions.

Burns, John F., "On the Heat of Dissociation of N_2", J. Chem. Phys., 23, 1347, (1955).

The author in this letter to the editor states that the most serious obstacle encountered in the application of electron impact methods to the measurement of dissociation energies is the inability to determine directly the state of electronic excitation of the resulting fragments. The retarding potential method of Fox, Hickam, Kjeldaas, and Grove (1951) was employed by the author to determine the excitation energy assignment and to investigate the ionization efficiency curve for the N^+ ion from N_2. Two of the resulting curves are shown in the article. Some thirty curves in all were obtained under varying instrumental conditions.

In all cases the first upward break occurred between 1.7 and 2.1 volts above onset, and the second between 0.4 and 0.7 volt above the first. It was concluded that both the atom and ion resulting from the dissociation of nitrogen under electron impact are formed in their ground states at onset. The first upward break at 1.9 electron volts was attributed to the process

$$N_2 \rightarrow N(^4S^0) + N^+(^1D) + e^-$$

and the second at 2.4 volts above onset to the process

$$N_2 \rightarrow N(^2D^0) + N^+(^3P) + e^-$$

Reference is made to the work of Clarke [Can. J. Phys., 32, 764, (1954)] who observed a single upward break at about 2.4 volts. Burns concluded that Clarke's inability to observe the first break at 1.9 volts was due to excessive energy spread in Clarke's electron beam.

Chamberlain, Joseph W., "The Ultraviolet Airglow Spectrum", Astrophys. J., 121, 277, (1955).

The main portion of the author's paper concerns the identification of the airglow bands from the forbidden Herzberg system of O_2 ($A\ {}^3\Sigma_u^+ \rightarrow X\ {}^3\Sigma_g^-$). It was shown in the present study that most of the airglow bands arise from the forbidden Herzberg System of O_2.

Reference is made to the observations obtained by M. Dufay (1953) who found that the weak twilight line at $\lambda 5200$ A was apparently due to the nebular transition of [N I]. Chamberlain states that the line is not detected in the nightglow and that it originates from an undertermined height in twilight, disappearing within two hours after sunset. According to Garstang [Astrophys. J., 115, 506, (1952)] the upper term for the [N I] doublet has a lifetime of 26 hours. The author concludes that it seems unusual that the daytime excitation does not persist during the night.

Christian, R. H., R. E. Duff, and F. L. Yarger, "Equation of State of Gases by Shock Wave Measurements. II. The Dissociation Energy of Nitrogen", J. Chem. Phys., 23, 2045 - 2049, (1955).

The authors state that the correct value of the dissociation energy for nitrogen is 9.764 ev and not 7.385 as formerly assumed. Reference is made to the work of Hendrie [J. Chem. Phys., 22, 1503, (1954)] which supports the higher value. Since the work of Kistiakowsky, Knight, and Malin [J. Am. Chem. Soc., 73, 2972, (1951)] was criticized because the conclusions depended on the assumption of the correctness of Chapman and Jouguet Theory of the detonation process and the existence of thermodynamic equilibrium in a very complicated system, the present investigation was undertaken with

precautions to circumvent these objections.

A detailed discussion is given of the shock wave calculations. The experimental results are presented in Table III of the paper. The authors conclude from the results of these experimental data on the equation of state measurements made behind strong shock waves that the dissociation energy of molecular nitrogen is 9.764 ev.

Douglas, A. E., "Recent Spectroscopic Studies of Simple Molecules", J. Phys. Chem., 59, 109, (1955).

This paper gives a brief summary of some recent investigations on the dissociations of O_2, N_2, CO, and CN. The author gives a brief summary of the work done on this topic at the Division of Physics of the National Research Council of Canada since 1952. Referring to the dissociation energy of N_2 reference is made to the discussion by Gaydon (1953) who gave strong evidence for a value of 9.756 ev for $D(N_2)$.

Unlike the spectrum of O_2, the spectra of N_2 do not yield direct proof of the dissociation of nitrogen. The spectra obtained do afford much data which can be readily interpreted if a value of 9.756 ev is assumed for the dissociation energy of molecular nitrogen. The author concludes that the present day data overwhelmingly favors a value of 9.756 ev for $D(N_2)$.

Ehler, A. W. and G. L. Weissler, "Absorption of Radiation in the Vacuum Ultraviolet by N Atoms Produced in a Discharge Plasma in Nitrogen", Phys. Rev., 98, 561, (1955).

This article is an abstract of a paper read at the 7th Annual Conference on Gaseous Electronics held 14-16 October 1954 at Washington Square College, New York. The absorption of electromagnetic radiation in the vacuum ultraviolet region of the spectrum produced in a discharge

plasma in N_2 was investigated. Densitometer traces of two photographic plate exposures (one with the Phillips Ionization Gauge discharge "on" and the other with the discharge "off") were made. In the spectral region λλ800-400 A the composite absorption cross section was found to be about $17 \times 10^{-18} cm^2$. Evidence from the experiments indicated that the significant absorbing component was atomic nitrogen. The absorption cross section of atomic nitrogen as found by analysis agreed with the theoretical value calculated by Bates and Seaton [Mon. Not. Roy. Astron. Soc., 109, 698, (1949)].

Ehler, A. W. and G. L. Weissler, "Ultraviolet Absorption of Atomic Nitrogen in its Ionization Continuum", J. Opt. Soc. Am., 45, 1035, (1955).

This paper describes a method which was developed by the authors for measuring absolute absorption coefficients of atomic nitrogen in the region of its ionization continuum below 800 A. The experimental procedure consisted in passing radiation from a spark discharge through the plasma of a Phillips Ionization Gauge discharge chamber. The spark source was an aluminum high-voltage electrode operated by a 2-kilowatt, 20,000-volts dc power supply which charged a condenser through a resistor. The condenser was arranged to discharge periodically into the light source.

In the interpretation of results the following mechanisms are given which may be responsible for the absorption continuum shown by the Phillips Ionization Gauge plasma.

	Reaction	Energy Required
(a)	$N_2^+ + h\nu \rightarrow N^+ + N$	8.7 ev (1420 A)
(b)	$N_2^+ + h\nu \rightarrow N_2^{++} + e^-$	34 ev (365 A)

	Reaction	Energy Required
(c)	$N + h\nu \rightarrow N^{+} + e^{-}$	14.54 ev (850 A)
(d)	$N^{+} + h\nu \rightarrow N^{++} + e^{-}$	29.6 ev (420 A)
(e)	$N_2^{*} + h\nu \rightarrow N_2 + e^{-}$	
(f)	$N_2^{M} + h\nu \rightarrow N_2^{+} + e^{-}$	
(g)	$N^{M} + h\nu \rightarrow N^{+} + e^{-}$	

Reaction (e) involving an excited molecule of nitrogen and reactions (f) and (g) involving the photoionization of a metastable molecule or atom were considered unlikely to occur.

In Part B of the paper the authors discuss the radiation from the light source which is passed through the plasma region after the Phillips Ionization Gauge discharge has been extinguished. It was concluded that only atomic nitrogen (N) and molecular nitrogen (N_2) could exist in the Gauge discharge chamber 0.1 millisecond after it had been turned off. It was also concluded that no ions either in excited or metastable states, could exist which indicated that atomic nitrogen was the absorber with a measured cross section of $12.8 \times 10^{-18} cm^2$.

Groth, W. E. and O. Oldenberg, "Dissociation by Impacts of The Second Kind", J. Chem. Phys., 23, 729-731, (1955).

This paper is an analysis of the photochemical dissociation of the nitrogen molecule by excited krypton. A mixture of krypton and nitrogen was intensely illuminated with a kryton lamp. Three possibilities of the impact are discussed: a. the atom transfer reaction; b. the stright chemical dissociation due to excitation of vibrational energy; and c. the dissociation due to the excitation of electronic energy of the molecule.

The authors conclude that the simplest interpretation is the production of a repulsive level of N_2 which at once dissociates. It is stated that the upper electronic levels of N_2 when excited by electron impact show little vibration. Reference is made to the "dissociation recombination" which contributes to the production of free nitrogen atoms.

$$N_2^+ + e^- \rightarrow N' + N'$$

This reaction was suggested by Bates [Phys. Rev., 78, 492, (1950)] for the mechanism of recombination of electrons and ions in the gas phase. The conclusion reached was that the dissociation of N_2 by excited Kr atoms involves the intermediate excitation of a repulsive level of the molecule which within the time of one vibration decomposes.

Hagstrum, Homer D., "Reinterpretation of Electron Impact Experiments in CO, N_2, NO, and O_2", J. Chem. Phys., 23, 1178, (1955).

Reference is made to an earlier paper by the author [Revs. Mod. Phys., 23, 185, (1951)] in which Hagstrum interpreted from electron impact data that D(CO) = 9.6 ev, D(N_2) = 7.4 ev, D(NO) = 5.3 ev, D(O_2) = 5.1 ev, and EA (O) = 2.2 ev. Recently the following values of D(N_2) = 9.76 ev, L(C) = 170 kcal/mole, and D(CO) = 11.1 ev are strongly indicated from several experiments. Using the values D(CO) = 11.1 ev, D(N_2) = 9.76 ev, D(NO) = 6.49 ev, and EA(O) = 1.45 ev one can calculate the appearance potentials, A_o, for ions of zero initial energy. These values are listed in Table I in the paper. The following values for A_o are given for N_2.

Process	Calculated A_o	Experimental A_o
$N_2(X\ {}^1\Sigma_g^+) + N^+({}^3P) + N({}^4S^0)$	24.30	24.3 ± 0.2 (N^+)

Hunten, D. M., "Some Photometric Observations of Auroral Spectra", J. Atm. Terrest. Phys., 7, 141-151, (1955).

The author in this paper reports that the observation was made on the "afterglow" type of aurora upon studying the $\Delta \nu = 2$ sequence of the second positive system of nitrogen. It was evident from the observation that the relative intensity of the Vegard-Kaplan bands 1-11 (3684 A) and 2-12 (3668 A) was greater than normal. Hunter suggested that a large concentration of excited molecules was built up during the bright auroral display, and that when the source of excitation ceased these molecules continued to radiate.

With reference to atomic nitrogen N I there is indirect evidence that the forbidden line at 5199 A behaves similarly. The forbidden line N I is nearly as strong as the 0-4 band of the N_2^+ negative system at 5228 A. It was pointed out that the photoelectric spectra had never shown any presence of the 5799 A line of N I.

The N I line would probably be present if it were one-tenth as strong as N_2^+ band. It was suggested that if the intensity of the N I line is smaller, then it should be present for a much larger fraction of the time than the other radiations.

Inn, Edward C. Y., "Vacuum Ultraviolet Spectroscopy", Spectrochim Acta, 7, 65-87, (1955).

This is an excellent review of the experimental methods and techniques in vacuum ultraviolet spectroscopy. There is emphasis on recent developments in g ating monochromators, background light sources, and photomultiplier detectors. Recently developed techniques for quantitative absorption spectrophotometry are discussed. The method for the measurement of ionization potentials and photoionization cross-section of molecules employed by the Geophysics Research Directorate of the Air Force

Cambridge Research Center is shown to be applicable to contribute to our knowledge of upper atmospheric constitutents and to provide the quantitative basis for studying absorption of solar radiation in the atmosphere. A list of 86 literature references is appended which greatly enhances the value of this review.

Jackson, D. S. and H. I. Schiff, "Mass Spectrometric Investigation of Active Nitrogen", J. Chem. Phys., 23, 2333, (1955).

In the introduction to this paper the authors make brief mention of the main features of the intense afterglow of nitrogen which was first observed by Lewis (1900). The main characteristics are: (a) its long duration; (b) its emission spectra consisting mainly of the first positive band of nitrogen involving the transition $B\ {}^3\Pi \rightarrow a\ {}^3\Sigma$ with intensity maximum at $v' = 6$ and 12; and (c) an enhanced chemical reactivity of the gas.

In the present investigation a mass spectrometer of a 90^{o} sector-type was used. The design of the instrument is described in full. The discharge tube employed to produce the active nitrogen was of the Wood-Bonhoeffer type with the gas outlet leading to the mass spectrometer located at the center of the discharge. A small central portion of an active nitrogen stream was sampled continuously into the mass spectrometer. It was observed, using argon as a calibrating gas, that the ratio of ion intensities of masses 14 to 28 was found to be higher than for ordinary nitrogen at the same pressure. The value of 14.7 ± 0.2 ev was obtained for the lower of the two appearance potentials. This was in close agreement with the ionization potential (14.54 ev) of the ground state ${}^4S/$ atom of nitrogen.

A second and higher appearance potential was observed at 16.1 ± 0.3 ev; different processes are suggested to explain it. The authors conclude that the ionization of ${}^4S$ atoms is the only process capable of explaining

the 14.7 ev appearance potential. The existence of ^4S atoms in active nitrogen is considered to be definitely established.

Kane, Walter R. and K. C. Clark, "Nitrogen Afterglow in a Magnetic Field", J. Chem. phys., 23, 859, (1955).

The authors have reported their study of the effect of a magnetic field on the exponential decay of a nitrogen afterglow at 0.017 mm pressure. A pulsed electrodeless discharge was employed to produce the afterglow. The light from the discharge tube was reflected to a distant 1P22 photomultiplier tube which was magnetically shielded. The afterglow was photographed on a calibrated oscilloscope. A trace of oxygen was used in the discharge tube.

A total of 95 decay transients with the magnetic field alternately present and absent was photographed. It was found that the magnetic field reduced the decay rate of the afterglow by 2.9 $\pm$ 0.5 percent. A theoretical discussion is included based upon kinetic theory calculations of the magnetic effect on the gas, thermalization of electrons, and electron attachment. It was concluded that the magnetic effect indicated that the energy released in ionic recombination contributed to the excitation of the short-lived afterglow.

Lee, Po., "Photodissociation and Photoionization of Oxygen (O_2) as Inferred from Measured Absorption Coefficients", J. Opt. Soc. Am., 45, 703-709, (1955).

As an addendum to this paper the absorption coefficients of N_2 in the wavelength region between 1050 and 910 A were measured. No measurable absorption was observed above 1040 A even at a pressure of 73 mm Hg. Below 1040 A there are the strong Worley bands. Since the absorption of N_2 is low, it was concluded from the present investigation that no absorption continuum of N_2 greater than 1 cm^{-1}

exists above 910 A.

A discussion is included on applications of some uses to which absorption coefficients may be put in the upper atmosphere. Two topics discussed are (a) the F-layers and the N_2-windows and (b) the E-layer and atmospheric windows. Reference is made to the computed curves relating absorption coefficients to layer heights of maximum absorption above 120 km by Clark [Phys. Rev., 87, 271, (1952)]. Figure 10 in the present paper shows the absorption of N_2 between 1050 and 900 A and indicates N_2-windows where the absorption is less than $1.6\ cm^{-1}$. Figure 11 in the paper shows the heights of maximum absorption of solar radiation by the major constituents of the ionosphere in the D, E, F_1, and F_2 regions.

Mange, P., "Diffusion Processes in the Thermosphere", Ann. geophys., 11, 153-168, (1955).

The author has added a brief paragraph on the topic of diffusion of atomic nitrogen in the thermosphere in order to make the subject of diffusion processes in the thermosphere complete. Reference is made to Nicolet [Rocket Exploration of the Upper Atmosphere, Ed. R. L. F. Boyd and N. J. Seaton, Pergamon Press, London, p. 361, (1954)] who analyzed the redistribution of atomic nitrogen formed through the process of photoionization of molecular nitrogen followed by dissociative recombination. Nicolet showed that the atomic nitrogen diffuses downward from the 160-km region where it is formed to lower altitudes where it may disappear as a result of three-body collisions.

Nicolet, Marcel, "The Aeronomic Problem of Nitrogen Oxides", J. Atm. Terrest. Phys., 7, 152, (1955).

In section II of this paper the dissociation of nitrogen molecules is discussed. Reference is made to the studies of Bates (1952) who considered the predissociation found by Herzberg and Herzberg (1948)

in the Lyman-Birge-Hopfield band system of nitrogen. Bate's value of the dissociation-rate coefficient is quoted for zero opitcal depth

$$J_{N_2} = 10^{-12} \text{ sec}^{-1}$$

Reference is also made to Mitra (1954) who used this value for J_{N_2} and calculated the effect of the optical depth, using a cross-section of 10^{-19} cm^2. Mitra found that the rate coefficient decreased rapidly downward with height in the mesosphere.

Another process for the dissociation of nitrogen molecules is discussed. It is pointed out that ultraviolet radiation of $\lambda < 796$ A and of shorter wavelengths $\lambda < 661$ A, for which according to Weissler, Lee, and Mohr (1952) the absorption coefficient is of the order of 2×10^{-17} cm^2 is able to ionize N_2. In addition the ionization of N_2 is possible by absorption of solar radiation from 175 A to shorter wavelength in the X-ray region. The following two values for the number of photons cm^{-2} sec^{-2} are quoted from data found by Byram, Chubb, and Friedman.

Spectral range	Number of photons
20 to 8 A	2×10^7 or 10^9
< 60 A	3×10^8 or 3×10^9

From these two divergent values the author deduced that the yield of nitrogen atoms through photoionization by ultraviolet radiation and X-rays leads to an even larger yield of nitrogen atoms than by the primary dissociation process.

It is also pointed out and emphasized that by the dynamic process of diffusion and mixing, the vertical distribution of atomic nitrogen after

its production is not dependent upon a dissociation equilibrium state but rather on atmospheric motions affecting a static equilibrium.

Nicolet, Marcel, "Nitrogen Oxides and the Airglow", J. Atmos. Terrest. Phys., 7, 297-309, (1955).

In this theoretical discussion of nitrogen oxides and the airglow the following reactions involving atomic nitrogen are considered.

$$N + NO_2 \rightarrow NO + NO$$

$$O + N + M \rightarrow NO + M$$

$$NO + h\nu \rightarrow N + O$$

$$NO + N \rightarrow N_2 + O$$

An assumption is made that the mean lifetime of a nitrogen atom is of the order of 1.5×10^5 sec at 50 km and 1.3×10^6 sec at 75 km. This implies that $n(NO) > n(N)$ which is considered to be correct below 90 km.

Omholt, A., "Intensity Measurements of the Second Positive Band System of Nitrogen in High-Latitude Aurorae", J. Atm. Terrest. Phys., 6, 61, (1955).

The author has reported some new measurements of the near-ultraviolet bands of the second positive band system (N_2, $C\ ^3\Pi_u \rightarrow B\ ^3\Pi_g$ The results are shown in Table 1 in the paper for the wavelengths λλ 4059, 3998, 3946, 3805, 3755, 3710, 3577, and 3537. The relative population rates $g(v')$ of the upper vibrational level are dervied for the $C\ ^3\Pi_u$ state of N_2 in the atmosphere during auroral displays. The mean relative values of the g's were found to be 1.00, 0.56, and 0.33.

Seaton, M. J., "Theories of the Airglow Spectrum", Ann. geophys., 11, 232-248, (1955).

This is a communication presented to the Assembly of the International Union of Geodesy and Geophysics held in Rome, September, 1954 under the auspices of the Committee of the Upper Atmosphere of the Association of International Geomagnetism and Aeronomy. The paper is also published in the I.A.G.A. Bulletin, No. 15b, Paris, (1956).

The author gives the following reaction as a possible excitation mechanism.

$$N(^4S) + N(^4S) + M \rightarrow N_2' + M''$$

This nitrogen recombination was originally suggested by Bates (1948) since oxygen recombination did not give sufficient energy for the excitation of a number of features in the airglow.

Under the topic "twilight phenomena", the [N I] line at λ 5199 A is discussed. Reference is made to Dufay [Ann. Phys., 8, 813, (1953)] who found that λ 5199 is emitted regularly at twilight with variable intensity. It was shown to be weaker in the morning than in the evening and less frequent in winter than in summer. That the emission is due to resonance seems probable. The effect of deactivation should not be overlooked. The effective duration of the "flash" is about 30 minutes as compared with 30 hours for the radiative lifetime of $N(^2D)$. It is concluded that the deactivation probability $d(^2D)$ is as great as 5×10^{-4} sec^{-1}.

The zenith intensity of λ 5199 according to Dufay corresponds to 2×10^7 photons cm^{-2} sec^{-1}. The number of nitrogen atoms required to give this intensity with resonance excitation is calculated to be at least 2×10^{19} per cm^2 column. The resonance mechanism would

require an extremely high degree of nitrogen dissociation, which is difficult to reconcile with the photochemical study of nitrogen dissociation of Bates [The Physics of the Upper Atmosphere, Ch. 12, The Solar Spectrum, edited by G. P. Kuiper, Vol. 2, University of Chicago Press, page 576, (1954)]. Bates suggested that excitation might result from dissociative recombination

$$N_2^+ + e^- \longrightarrow N' + N''$$

The lack of correlation between λ 5199 and N_2^+ is an objection to the above excitation mechanism; Dufay found that N_2^+ is correlated with magnetic activity while λ 5199 is not.

Stanley, C. R., "A New Phenomenon Associated with Active Nitrogen", Proc. Phys. Soc. (London), 68A, 709-716, (1955).

The author describes the appearance of an orange glow protruding from a hole in a hollow electrode during his attempt to excite a fluorescence in nitrogen by means of a high-voltage arc with a hollow electrode. The spectrum of the beam was photographed under various conditions with Hilger medium quartz and medium glass spectrographs. The 1st positive, 2nd positive and 1st negative band systems of nitrogen appeared on the spectrogram with an intensity distribution resembling that of an ordinary discharge spectrum.

The following features were studied: a. comparison of exciting arc, beam, and chamber glow, b. effect of pressure variation, c. effect of current variation, d. physical nature of the beam, e. active nature of the beam, and f. determination of the attenuation constant of the beam.

The mechanism of production of the 1st positive bands is suggested to be due to the presence in the beam of a large concentration of $N_2(A)$ molecules together with ordinary active nitrogen. If the active nitrogen is con-

sidered to consist of atomic nitrogen, then the author proposes that recombination of two nitrogen atoms in a three-body collision with an $N_2(A)$ molecule would release the energy necessary to raise the molecule to the B state from which radiation of the 1st positive system results.

Stewart, D. T., "Electron Excitation Functions of Infrared Nitrogen Spectra", Proc. Phys., Soc. (London), A68, 404-408, (1955).

The author has determined by means of photographic photometry the relative excitation function of lines and bands in the near infrared spectrum of nitrogen. The maximum of the (2, 0 and 3, 1) Meinel bands of N_2^+ are reported to occur at 60 volts. The N I lines occur at 8200 A, resulting from the transition $3s^4P \longrightarrow 3p^4P^0$ occur at 90 volts.

It was noted that in the low pressure range the atomic nitrogen (N I) lines were observed for electron energies of 24 volts or lower. This was considered to be not incompatible with an energy of dissociation of 9.76 ev for $X\ ^1\Sigma_g^+ N_2$ and an excitation potential for the $3p\ ^4P^0$ from the ground state of N.

Stewart, D. T. and K. G. Emeleus, "Note on an Experiment by Rayleigh on Active Nitrogen", Trans. Faraday Soc., 51, 491-492, (1955).

Reference is made to the experiments of Lord Rayleigh in which active nitrogen was produced under well-defined electrical conditions and was compared with yields from different sections of a d. c. low-pressure glow discharge. The yield was found to be greatest near the cathode and diminished along the negative glow. A frequent assumption made is that the activity of the cathode sections is due to the negative glow.

The authors point out that this assumption gives rise to difficulties in the interpretation of the Lewis-Rayleigh afterglow if the view is adopted that it is connected with nitrogen atoms, since the visible arc spectrum

of nitrogen N I is normally absent from the negative glow. Visible N I lines have been shown to be intensely emitted from the cathode glow.

The negative glow emits N I lines thus showing the presence of N^+. The authors state that visible lines of N I are relatively difficult to produce and that the most intense part of the spectrum normally obtained is in the near infrared. In the present investigation the infrared N I spectra of a number of d.c. glow discharges of nitrogen were photographed at pressures of about 1 mm and not preactivated. Infrared N I lines were emitted in all cases from the negative glow. It was concluded that some dissociation of N_2 to atomic nitrogen definitely exists in the negative glow.

Tanaka, Yoshio, "Absorption Spectrum of Nitrogen in the Region from 1075 to 1650 A", J. Opt. Soc. Am., 45, 663, (1955).

The author in the present paper states that the so-called Lyman-Birge-Hopfield bands are the only known absorption bands of the nitrogen molecule in the ultraviolet region above 1000 A. Reference is made to absorption measurements of nitrogen in the vacuum region by Weissler and his co-workers (1952), and to Watanabe and his co-workers (1953). The absorption coefficients reported by the former workers were fairly high. The purpose of the present investigation was to find Weissler's absorptions photographically and to reinvestigate the absorption bands of nitrogen using argon continuum as a background.

The author was unable to find in his experiments the absorption reported by Weissler. If the latter's absorptions were due to molecular nitrogen, Tanaka concluded that they should have been observed in the present investigation since an absorbing layer of N_2 about 400 times greater was used. Below 1130 A four bands were observed at 1123, 1099, 1089, and 1076 A. Three of these were interpreted to be the first

bands of the transition

$$C\ {}^3\Pi_u \longleftarrow X\ {}^1\Sigma_g^+ .$$

Toennies, J. P. and E. F. Greene, "Dissociation of Nitrogen in Shock Waves", J. Chem. Phys., 23, 1366, (1955).

Reference is made to the work of Kistiakowsky, Knight, and Malin [J. Chem. Phys. 20, 876, (1952)], of Hendrie [J. Chem. Phys., 22, 1503, (1954)], and of A. E. Douglas [J. Phys. Chem., 59, 109, (1955)] who have shown reasonable agreement from a variety of experiments that the value of

$$D(N_2) = 225 \text{ kcal per mole.}$$

The authors describe in the present paper their results from the study of the properties of strong shock waves in nitrogen. Their investigations support the so-called high value for the dissociation of nitrogen.

Varney, R. N., "Reactions of Nitrogen Activated by Electric Discharge", J. Chem. Phys., 23, 866-868, (1955).

The purpose of the experiments reported in this paper was to test the roles of excitation and of ionization of nitrogen in activating it, that is, rendering the nitrogen capable of reacting directly with H_2, O_2, CH_4, and CO. It was concluded from this study of the simple chemical processes involving nitrogen in discharge reactions that the reactions depended only on activating the N_2 to some non-ionized state, and neither on nitrogen ions nor on direct excitation of the other reacting gas.

Wainfan, N., W. C. Walker, and G. L. Weissler, "Photoionization Efficiencies and Cross Sections in O_2, N_2, CO_2, A, H_2O, H_2, and CH_4", Phys. Rev., 99, 542, (1955).

This is a report of the measurements of the absolute photoionization cross sections and ionization efficiencies of various atmospheric gases as a function of wavelength between 473 and 1020 A. The three components in the instrumentation were a light source and normal incidence vacuum monochromator, instruments for determining the absolute light intensity at the exit slit, and an assembly of ion chambers, mounted in a gas-failled experimental chamber behind the exit slit, in which the ionization currents and absorption coefficients were measured.

With reference to nitrogen the results are compiled in Table III of the paper. The ionization efficiency was found to increase rapidly to nearly 100 percent from an onset at 792 $\pm$ 5 A to about 700 A. At shorter wavelengths the entire absorption mechanism appeared to be photoionization. The onset limit at 792 $\pm$ 5 A corresponded to a first ionization potential of 15.6 $\pm$ 0.1 volts. Reference is made to the work of Hagstrum (1951) who reported the ionization limit of 796 A or 15.58 volts for the transition

$$N_2\ (X\ {}^1\Sigma_g^+) \longrightarrow N_2^+\ (X\ {}^2\Sigma_g^+) + e^-$$

1956

Bass, Arnold M. and Herbert P. Broida, "Spectra Emitted from Solid Nitrogen Condensed at 4.2°K from a Gas Discharge", Phys. Rev., 101, 1740-1747, (1956).

The products of an electrical discharge in a stream of flowing nitrogen gas were frozen at the temperature of liquid belium. It was observed that the solid material emitted a glow. The spectra from

the solid nitrogen are very different from those obtained from either the nitrogen discharge or the nitrogen afterglow.

The spectral range studied was in the region 2200 to 7000A. A detailed description of the apparatus is given as well as the visual and spectroscopic observations. Table I in the paper gives a list of the observed lines and bands emitted by the solid composed of condensed products of a discharge through nitrogen gas. There is evidence that the observed glows are a solid phenomenon.

Berkowitz, Joseph, William A. Chupka, and G. B. Kistiakowsky, "Mass Spectrometric Study of the Kinetics of Nitrogen Afterglow", J. Chem. Phys., 25, 457-466, (1956).

This paper is a report of experiments upon the nature of the Lewis-Rayleigh afterglow in nitrogen. These experiments were designed to simultaneously examine the afterglow with a mass spectrometer and a photomultiplier. The object was to correlate the magnitude of some mass peaks with the afterglow intensity. Details are given of the arrangement of the apparatus and the mass spectrometer. The experimental results are discussed under the headings: a. nature of the active particles; b. kinetics; c. temperature effect; d. pressure effect; e. effect of oxygen; f. nitric oxide effect; and g. determination of absolute concentrations and intensities.

The conclusions derived from the experimental data are first, that the mechanism of the airglow involves three-body collisions as the rate determining step, and second, that the reaction involves two ^4S nitrogen atoms.

Two mechanisms are given for the afterglow. In mechanism II which is the preferred one, the intermediate formation of the $^5\Sigma_g^+$ molecule state followed by a collision-induced radiationless transition into the

$^3\Pi_g$ state is considered probable. A potential energy diagram of the pertinent electronic states of the nitrogen molecule is included in the paper.

Mechanism II

$$N + N + M \longrightarrow N_2^{**} + M \; ; K_1$$

$$N_2^{**} + M \longrightarrow N + N + M \; ; K_2$$

$$N_2^{**} + M \longrightarrow N_2^{*} + M \; ; K_3$$

$$N_2^{*} \longrightarrow N_2^{1} + h\nu \; ; K_4$$

$$N_2^{**} \longrightarrow N_2^{1} + h\nu \; ; K_5$$

$$N_2^{*} + M \longrightarrow N_2^{x} + M \; ; K_6$$

N_2^{**} denotes a molecule of N_2 in the $^5\Sigma_g^+$ state, N_2^{*} a nitrogen molecule in the B $^3\Pi_g$ state, N_2^{1} one in the A $^3\Sigma_u^+$ state, and N_2^{x} that in a further specified state from which no visible afterglow is emitted.

Branscomb, Lewis, M. and Stephen J. Smith, "Electron Affinity of Atomic Sulfur and Empirical Affinities of the Light Elements", J. Chem. Phys., 25, 598, (1956).

The threshold for ejection of an electron from an unexcited atomic negative ion by absorption of a photon is energetically equivalent to the electron affinity of the neutral atom. The authors state that from their study of electron photodetachment from a beam of O^- ions in high vacuum a value of 1.48 ± 0.10 ev was obtained for the electron affinity of atomic oxygen. In the present investigation the electron affinity of atomic sulfur was

found to be 2.07 ± 0.07 ev. Reference is made to Bates and Moiseiwitsch [Proc. Phys. Soc. (London), A68, 540, (1955)] who predicted a value of 2.1 ev affinity for atomic sulfur.

With reference to atomic nitrogen the authors state that N^- ions have not been observed and are presumed to be unstable.

Broida, H. P. and O. S. Lutes, "Abundance of Free Atoms in Solid Nitrogen Condensed at 4.2°K from a Gas Discharge", J. Chem. Phys., 24, 484-485, (1956).

Reference is made to a former paper by Broida and Pellam [Phys. Rev., 95, 845, (1954)] in which evidence was obtained for the presence of nitrogen atoms in the solid condensed at 4.2°K from a nitrogen gas discharge. It was observed that a glow appeared during the operation of the discharge and also an afterglow which persisted for several minutes, followed by a blue afterglow which appeared at some higher temperature (28°K - 35°K) during warm-up of the apparatus.

The authors state that an estimate of the abundance of nitrogen atoms in the solid can be obtained from the measured temperature change, ΔT, associated with the recombination. Using average values for specific heats over the temperature interval of warm-up, the authors found that the total heat absorbed was about 47 calories of which 8 and 29 calories were required for heating the glass collection chamber and solid nitrogen, respectively, and 10 calories for the phase change in molecular nitrogen at 35.6°K. Taking the heat of dissociation of nitrogen to be 225 kilocalories per mole, the concentration of nitrogen atoms in the solid was determined to have a value of 0.2 percent.

Ditchburn, R. W., "Absorption of Ultraviolet Radiation by the Atmospheric Gases", Proc. Roy. Soc., A236, 216-226, (1956).

The author classified absorption of radiation by gases at low pressures into two types: absorption continua associated with photodissociation and photoionization of the gases; and line absorption and band absorption which produces excited atoms or molecules. Figure 29 in the paper gives absorption continua of N_2, O_2, N, O, and O_3 in the spectral range 3000 to 200 A as a function of photo-energy.

Nirtrogen is considered to be effectively transparent above 1200 A, within the spectral range 920 to 200 A coressponding to a penetration height of 125 to 150 km. [The penetration height (H_p) is defined as that height at which radiation of a given photon energy would be attenuated to a fraction e of the original value.] The following data obtained for N_2 and N.

$N_2 \rightarrow N_2^+$ (threshold 800 A, the absorption coefficient, α, varies from 500 to 1000 cm^{-1})

$N \rightarrow N^+$ (threshold 850 A, the absorption coefficient, α, was calculated by Bates and Seaton [Mon. Nat. Roy. Astron. Soc., 109, 698, (1949)] to be about 250 cm^{-1} in pure N.

Evans, H. G. V. and C. A. Winkler, "The Reactive Components in Active Nitrogen and the Role of Spin Conservation in Active Nitrogen Reactions", Can. J. Chem., 34, 1217-1231, (1956).

Evidence is presented in this extensive survey of the available experimental information that atomic nitrogen is the main reactive species in active nitrogen. The authors state that the $A\ {}^3\Sigma$ state should be the longest-lived electronically excited state of molecular nitrogen. They observed also that during the emission of the Lewis-Rayleigh afterglow

of active nitrogen the A $^3\Sigma$ state is formed continually in small amounts, since it is the B $^3\Pi \longrightarrow$ A $^3\Sigma$ transition that gives the afterglow.

The authors call attention to the fact that under special experimental conditions, other afterglows in nitrogen may be obtained. It is pointed out that the spectrum of the so-called "auroral" afterglow contains the forbidden Vegard-Kaplan bands in N_2 in the metastable a $^3\Sigma$ state and also forbidden lines of atomic nitrogen in the metastable ^2P state, whereas the Lewis-Rayleigh afterglow does not show either of these spectra. This was interpreted to mean that neither of these metastable species is present in significant concentration in active nitrogen.

Evidence is cited indicating the presence of more than one active species of nitrogen as well as the presence of vibrationally excited molecules. The topic of the role of spin conservation in nitrogen atom reactions is considered and shown to lead to the conclusion that reactions which conserve spin occur more readily than those in which spin is not conserved. A bibliography of 75 literature references of previous investigations is appended.

Evans, H.G.V., G. R. Freeman, and C. A. Winkler, "The Reactions of Active Nitrogen with Organic Molecules", Can. J. Chem., 34, 1271-1287, (1956).

Reference is made in the introduction to the discovery of active nitrogen by Lewis in 1900. Reference is also made to the extensive studies of the physical and chemical properties of active nitrogen by Strutt (later Lord Rayleigh). Rayleigh observed that all the reactions of active nitrogen with organic compounds were accompanied by the brilliant emission of the CN spectrum. For ten years workers at the Physical Chemistry Laboratory of

McGill University have been conducting investigations on the reactions of active nitrogen with various types of molecules. The present paper gives the main features of the reaction of active nitrogen with various organic compounds.

The compounds considered are the unsaturated hydrocarbons (ethylene, acetylene, prophylene, and butenes), saturated hydrocarbons (methane, ethane, propane, butanes, and neopentane), cycloparaffins, alkyl chlorides, methyl cyanide, and methylamine.

An extensive discussion is given of reaction mechanisms on the basis that atomic nitrogen is responsible for the reactions of active nitrogen with organic molecules. Interpretations are based upon the acceptance of the high value 9.76 ev for $D(N_2)$. A bibliography of 55 references is included in the paper.

Frost, D. C. and C. A McDowell, "The Dissociation Energy of the Nitrogen Molecule", Proc. Roy. Soc. (London), <u>A236</u>, 278-284, (1956).

The authors discuss three ways by which the atomic nitrogen ions are produced, those in which the accompanying nitrogen atom is produced in its three states, $^4S^0$, $^2D^0$, and $^3P^0$. The atomic nitrogen ion is always formed in its ground state (^3P). From the appearance potentials it is concluded that the dissociation energy of nitrogen is 9.756 ev. In arriving at this conclusion the following processes are considered.

$$N_2 + e^- = N^+ + N + 2e^- \qquad (a)$$

$$N_2(^1\Sigma_g^+) + e^- = N^+(^3P) + N(^4S^0) + 2e^- \qquad (a1)$$

$$D(N_2) = V(N^+) - I(N) \qquad (b)$$

$$N_2(^1\Sigma_g^+) + e^- = N^+(^3P) + N(^2D^0) + 2e^- \qquad (c)$$

$$N_2(^1\Sigma_g^+) + e^- = N^+(^3P) + N(^2P^0) + 2e^- \qquad (d)$$

$$N_2(^1\Sigma_g^+) + e^- = N^+(^1D) + N(^4S^0) + 2e^- \qquad (e)$$

$$N_2(^1\Sigma_g^+) + e^- = N^+ (^1S) + N(^4S^0) + 2 e^- \quad (f)$$

$$N_2(^1\Sigma_g^+) + e^- = N^+ (^3P) + N(^2D^0) + 2 e^- \quad (g)$$

$$N_2(^1\Sigma_g^+) + e^- = N^+ (^1S) + N(^2D^0) + 2 e^- \quad (h)$$

$$N_2(^1\Sigma_g^+) + e^- = N^+ (^3P) + N(^4P) + 2 e^- \quad (i)$$

Each of the processes is discussed. From the equation

$$D(N_2) = V(N^+) - I(N)$$
$$24.32 \text{ ev} - 14.54 \text{ ev}$$

where $V(N^+)$ is the appearance potential of the N^+ ions, and I(N) is the ionization potential of the nitrogen atom the value of 9.78 ev for $D(N^2)$ is deduced.

Gromova, I.I., "The Photodissociation of Nitrogen", Optika i Spektroskopiya, 1, 433-434, (1956).

A potential energy diagram is given for the X $^1\Sigma_g^+$, A $^3\Sigma_u^+$, B $^3\Pi_g$, C $^3\Pi_u$, and a $^1\Pi_g$ energy levels. These were calculated from the Hulbert-Hirschfelder formula. It is stated that an analysis of the curves appears to indicate the probability that nitrogen molecules which are in the a $^1\Pi_g$ state in the region of intersection with the A $^3\Sigma_u^+$ level would dissociate according to the A $^3\Sigma_u^+$ potential curve into two normal nitrogen atoms in the ^4S state. Among the literature references the papers by Tanaka [J. Opt. Soc. Am., 45, 663, (1955)] and Douglas and Herzberg [Can. J. Phys., 29, 294, (1951)] are cited in the bibliography.

Harteck, P. and S. Dondes, "Nitrogen Oxide Dosimeter for High Levels of Batas, Gammas, and Thermal Neutrons", Nucleonics, 14, No. 3, 66-72, (1956).

The authors give the following as the main reactions in the de-

composition of nitrous oxide by ionizing radiation.

$$N_2O \longrightarrow N_2O^* \longrightarrow N_2 + O \sim 80\%$$

$$N_2O \longrightarrow N_2O^+ + e^- \longrightarrow N + NO \sim 20\%$$

$$2NO + O_2 = 2\ NO_2$$

$$NO_2 + N \longrightarrow 2\ NO \longrightarrow N_2O + O \longrightarrow N_2 + O_2$$

$$N_2O^+ + NO = N_2\ O + NO^+$$

$$NO^+ + e^- = N + O \text{ or } NO + h\nu$$

The authors state that the decomposition of N_2O by ionizing radiation is temperature independent, and that the lower temperature of usefulness is limited by the vapor pressure of N_2O which at -81°C is one atmosphere. At 200°C nitrous oxide is indefinitely stable to thermal decomposition and thus for short-time irradiation temperatures about 200°C could be used. The thermal decay constant is given as $K = 4.2 \times 10^9\ e^{-53,000/rT}\ sec^{-1}$.

Harteck, P. and S. Dondes, "Producing Chemicals With Reactor Radiations", Nucleonics, 14, No. 7, 22-25, (1956).

In Table 2 of this paper Harteck and Dondes give a list of 27 reactions between atomic nitrogen, atomic oxygen, and combinations which are available. These are fully discussed in another paper by the authors.

Herman, L., J. Morel, and R. Herman, "Emission du Spectre de L'Azote dans les Aurores de Haute Altitude", "Emission of the Spectrum of Nitrogen in Auroras of High Altitude", Ann. Geophys., 12, 228-231, (1956).

The authors have studied the intensity of N_2 bands emitted by the aurora borealis and have found it to depend on the population of the excited states and the rate at which they are deactivated by nonradiative processes. At altitudes below 100 km deactivation of nitrogen molecules in any of the states C $^3\Pi$, B $^3\Pi$, and A $^3\Sigma$ by electron impact is negligible in comparison with that by molecular impact. In auroras above 100 km electronic deactivation becomes important.

Herzfeld, C. M. and H. P. Broida, "Interpretation of Spectra of Atoms and Molecules in Solid Nitrogen Condensed at 4.2^{o}K", Phys. Rev., 101, 606-611, (1956).

In the experiments reported in this paper nitrogen gas at low pressure was passed through an electric discharge and condensed at 4.2^{o}K. The emission spectra from the solid was explained by assuming that a large number of nitrogen atoms were deposited during the process. Table I in the paper gives a list of the lines emitted from the condensed solid nitrogen, and Figure 1 gives a typical spectrum of the condensed products.

The long persistent blue-green spectral emission was interpreted as due to the transition of nitrogen atoms from the metastable ^{2}D state to the ground state ^{4}S. Reference is made to the historical experiments of Vegard, McLennan, and Shrum (1924) who first observed the α and β lines in the spectrum of solid nitrogen.

Lofthus, Alf , "Emission Band Spectra of Nitrogen. The Lyman-Birge-Hopfield System", Can. J. Phys., 34, 780-789, (1956).

This paper describes a study of the near ultraviolet emission spectrum of nitrogen photographed under high resolution. Thirteen bands of the a $^1\Pi_g$ - X $^1\Sigma_g^+$ system (Lyman-Birge-Hopfield) were analyzed. New data on vibrational and rotational constants were obtained. Predissociation in the a $^1\Pi_g$ state was observed and studied. The predissociation limit was found to be 78828 $\pm$ 50 cm^{-1}.

Meadows, Edith B. and John W. Townsend, Jr., "Neutral Gas Composition of the Upper Atmosphere by a Rocket-Borne Mass Spectrometer", J. Geophys. Research, 61, 576-577, (1956).

In this paper the authors give a preliminary report on the night-time flight of a mass spectrometer designed to investigate the composition of the upper atmosphere. The mass spectrometer was the Bennett radio-frequency type. The spectrum showed peaks at mass numbers 44, 40, 32, 16, 28, 14, 18, and two others at 46 and 23. The atomic ions, O^+ and N^+ at mass numbers 16 and 14 are formed within the ion source. The authors point out that this does not necessarily indicate the presence of atomic oxygen and atomic nitrogen in the ambient upper atmosphere. The peak of the flight was 141.6 km.

Rao, K.S. Raghavendra, "Active Nitrogen", J. Karnatak Univ., Dharwar, India, No. 1, 143-156, (1956).

A review of experiments and theories are summarized and discussed under the following topics.

1. Introduction
   (a) Historical
   (b) Production and properties

2. The Characteristic features

   (a) Spectrum

   (b) Energy content

   (c) Negative temperature coefficient

   (d) Ionization

   (e) Laws of decay

   (f) Kaplan's afterglow

3. The theories

   (a) Early atom theory

   (b) Metastable molecule theory

   (c) Ionic theory

   (d) Metastable atom theory (Mitra)

   (e) Atom theory (Oldenberg)

4. General remarks

5. Bibliography

In the historical introduction reference is made to Warburg who in 1884 observed that an electrical discharge tube containing nitrogen at low pressure continued to glow after the electric current was turned off. This glow is called the afterglow. A list of 39 literature references is included, the most recent of which is Stewart and Emeleus [Trans. Faraday Soc., 51, 491, (1955)].

Stewart, D. T., "Spectroscopic Evidence of Atoms in Active Nitrogen", Proc. Phys. Soc. (London), 69B, 956-957, (1956).

Nitrogen has low metastable ^2D and ^2P states with excitation potentials of 2.4 and 3.6 volts respectively. It is possible that the forbidden radiative transitions between these and the ground state might be detectable. A brief description is given of the instrumentation. The spectrum was photographed with a quartz prism spectrograph. An isolated line with wavelength 3466.5 $\pm$ 0.3 A was recorded in the pressure range 2 to 10 mm Hg. The intensity distribution in the first positive bands was typical of active nitrogen; there was no correlation

between the intensity of the line 3466 A and the intensities of the NO bands. It was concluded that the 3466 A line was the unresolved doublet N I, and that nitrogen atoms in the ^2P state were present in the afterglow. It was r shown that nitrogen atoms in the three low energy level states (. , ^2D, and ^4S) are produced in the parent discharge by dissociative ionization.

Thorburn, R. and J.D. Craggs, "Electron Impact Studies of the Dissociation Energies of N_2 and H_2", Proc. Phys. Soc. (London), 69B, 682-685, (1956).

The authors state that their present work was prompted by the existence of widely differing values for $D(N_2)$. Reference is made to Gaydon [Dissociation Energies, London, Chapman and Hall, (1947)] who discussed the three most likely values (9.764, 8.573, and 7.383 ev) for the energy dissociation of nitrogen and stated that the first appeared most likely.

The mass spectrometer was a 60^o Nier-type and the Lozier apparatus was employed. The first measurement was used to measure the positive ion current as a function of electron energy, and the positive ion current as a function of the retarding potential was determined in the Lozier apparatus. The mass spectrometer was used to identify the particular ion occurring at some "break" on the ionization curves.

In nitrogen there was a break corresponding to the formation of N_2^+ in the reaction

$$N_2 + e^- \longrightarrow N_2^+ + 2e^-$$

The appearance potential of the N_2^+ ions corresponded to the ionization potential of nitrogen, 15.7 ev. The appearance potential for the process yielding N^+ in the Lozier apparatus was obtained from this value by the

method of extrapolated linear intercepts. The $A(N^+)$ value was found to be 24.3 ± 0.3 ev. The value of 9.764 ev for $D(N_2)$ was supported by the present investigation.

Watanabe, K. and F.F. Marmo, "Photoionization and Total Absorption cross Section of Gases. II. O_2 and N_2 in the Region 850 - 1500 A", J. Chem. Phys., 25, 965-971, (1956).

This paper is an extension of studies by Watanabe and others [Geophysical Research Paper, No. 21, Geophysics Research Directorate, (1953)] on absorption coefficients of oxygen, nitrogen, and other atmospheric gases. The region 850 to 1100 A is of importance to the theory of atmospheric E layer formation. Four immediate objectives of the present work are: a. to obtain quantitative absorption coefficients and ionization cross sections of O_2 and N_2; b. to establish the preionization of Hopfield bands of O_2 in the 900 to 1000 A region; c. to determine the first ionization potential of O_2 by the photoionization method; and d. to detect any absorption continuum of N_2.

The symbol notations are given as follows. The absorption coefficient k (or k value) in cm^{-1} expresses the intensity of absorption. The intensity is also expressed by the cross section, symbolized by σ in cm^2. $I = I_o \exp(-kx)$ where I_o and I are the incident and transmitted light intensities, and x in cm is the thickness of the absorbing gas layer reduced to NTP. The cross section is defined by the equation $\sigma = k/n_o$ where n_o equals 2.69×10^{19} particles cm^{-3}.

The experimental method and technique are those used previously by these investigators. The changes in arrangement of the apparatus are described. In the case of nitrogen a micromanometer and an oil manometer were used for pressure measurements.

With respect to the absorption intensity of N_2 in the region 850 to 1100 A it is stated that the absorption spectrum of N_2 consists for the most part of sharp bands. Figure 2 in the paper is a semilog graph (λ vs apparent k value) of the absorption spectrum of N_2 obtained with a resolution of about 1 A. Measurements were made for 13 pressures from 0.066 to 3.44 mm Hg. With refernce to the question as to whether there are any absorption continua within this spectral region (850 to 1000 A) the authors state that their results are in agreement with those of Lee, [J. Opt. Soc. Am., 45, 703, (1955)] who finds that it is not possible to establish the presence of a continuum.

Wilkinson, P.G., and N.B. Houk, "Emission Spectra of Nitrogen in the Vacuum Ultraviolet", J. Chem. Phys., 24, 528-534, (1956).

The authors report that they have photographed the emission spectra of nitrogen in the vacuum ultraviolet. Bands of the $b' \, ^1\Sigma_u^+ - X \, ^1\Sigma_g^+$ and the $a \, ^1\Pi_g - X \, ^1\Sigma_g^+$ systems were analyzed. New rotational and vibrational constants were obtained. A new predissociation is reported at 13.233 ev. The predissociation of $b' \, ^1\Sigma_u^+$ was considered to be compatible with either the 9.756 or the 7.373 ev value for the dissociation energy of nitrogen.

Woolley, Harold W., "Thermodynamic Properties of Gaseous Nitrogen", National Advisory Committee for Aeronautics Technical of Standards, Technical Note 3271, 114 pp, (1956).

This comprehensive series of tables of the thermal properties of molecular nitrogen was prepared in an NBS-NACA series. They include the thermodynamic functions for the gas, both real and ideal, the transport properties for the gas, and the vapor pressure of the liquid and the solid.

The bibliography contains 96 references, The content of the tables of data is listed as follows:

Table 1. Specific heat, enthalpy, entropy, and free energy of molecular nitrogen in ideal-gas state.

Table 2. Specific heat, enthalpy, entropy, and free energy of atomic nitrogen in ideal-gas state.

Table 3. Compressibility factor $Z = PV/RT$ for molecular nitrogen.

Table 4. Density ρ/ρ_o of molecular nitrogen.

Table 5. Specific heat C_p/R of molecular nitrogen.

Table 6. Enthalpy $(H - E_o^o)/RT_o$ of molecular nitrogen.

Table 7. Entropy S/R of molecular nitrogen.

Table 8. Specific heat ratio $\gamma = C_p/C_v$ of molecular nitrogen.

Table 9. Sound velocity a/a_o in molecular nitrogen.

Table 10. Coefficient of viscosity η/η_o of molecular nitrogen.

Table 11. Thermal conductivity k/k_o of molecular nitrogen.

Table 12. Prandtl number $N_{P_r} = \eta C_p/k$ of molecular nitrogen at atmospheric pressure.

Table 13. Vapor pressure of nitrogen.

Table 14 and 15 give the values of the virial coefficients and their first derivatives.

Several tables of conversion factors to frequently used units and graphical representation are also included.

1957

Anderson, J. M., "The Nature of Active Nitrogen", Proc. Phys. Soc. (London), 70A, 887-899, (1957).

It is shown in the present paper that the first bimolecular process, found experimentally, in the decay of the nitrogen afterglow requires oxygen

as a catalyst, and that both active bodies are drawn from a common population. The activation energy necessary for the afterglow process is 900 cm^{-1}. A second bimolecular process involves two active bodies having monomolecular decays and being drawn from different populations. Only negligible activation is needed for this afterglow process. A final monomolecular decay shows usual diffusion collision pressure dependence at higher temperatures and effective diffusion collision dependence only at lower temperatures.

In the introduction mention is made of the many theories which attempt to account for the glow. Six properties are listed for which a satisfactory theory must account. In order to analyze the problem three assumptions were adopted. a. Two energy carrying particles interact together. b. This interaction results in the emission of one afterglow quantum. c. The energy carriers individually give up their energy without visible radiation simultaneously with this process which is assumed to be monomolecular.

The first process is thought to be a recombination of nitrogen atoms with molecular oxygen, a few parts per million, as a catalyst. The second process is considered to be a collision of two different vibrationally excited ground states of nitrogen molecules with molecular hydrogen, a few parts per million, as a catalyst.

Astoin, Nicole, and Janine Granier, "Sur Le Spectre D'absorption de L'Azote dans L'Ultraviolet Extreme", "Absorption Spectrum of Nitrogen in the Extreme Ultraviolet", Compt. rend., 244, 1350-1353, (1957).

This is a report of the N_2 absorption spectrum in the 150 to 1000-A spectral region. The pressure range was from 2 to 6 x 10^{-2} mm.

Figures 1 and 2 show several blending continua of apparent continuous absorption. These continua are interpreted in terms of the ionization and dissociation of N_2. Two mechanisms for the dissociation of molecular nitrogen are given.

$$N_2 \rightarrow N^+(^4S) + N(^3P)$$

$$N_2 \rightarrow N(^2P) + N^{++}(^4P)$$

A bibliography of twelve references to previous investigations by other workers is included.

Aziz, Farhart and Elias Dubash, "Laboratory Method for Obtaining Oxygen Free Nitrogen from Air", Pakistan J. Sci. Research, 9, 83-84, (1957).

The authors report that oxygen-free air may be obtained by passing air through ammonia water and then through a tube containing copper turnings heated to 600 to 800°. The final traces of oxygen are removed by passage through Badger reagent which consists of a saturated solution of ammonium chloride in equal parts of ammonia water and water containing pieces of copper wire. Finally passage through concentrated sulfuric acid removes the last traces of ammonia.

Barth, Charles A. and Joseph Kaplan, "Herzberg Oxygen Bands in Air Afterglows and the Night Airglow", J. Chem. Phys., 26, 506-510, (1957).

A brief discussion of the apparatus employed and the method of procedure is given. In the discussion portion of the paper the authors have considered various accepted mechanisms for producing nitrogen in order to decide on the most probable mechanism for producing the Herzberg bands.

According to accepted theories the Lewis-Rayleigh afterglow involves atomic nitrogen recombination

$$N + N + M \rightarrow N_2{}^* + M$$

Reference is made to the experiments of Tanaka who observed that the blue nitric oxide afterglow was produced by atomic nitrogen and atomic oxygen recombining over nitric oxide

$$N + O + NO \rightarrow NO + NO^*$$

The following mechanism is given

$$N + O_3 \rightarrow NO + O_2{}^*$$

to explain production of the excited oxygen molecules which emit the Herzberg bands. The reaction of atomic nitrogen with nitrogen dioxide is also cited as having enough energy (5.31 ev) to excite the Herzberg bands.

$$N + NO_2 \rightarrow N_2 + O_2$$

With reference to the night afterglow the reaction of atomic nitrogen with ozone is given as a possible mechanism for contributing to the Herzberg bands.

$$N + O_3 \rightarrow NO + O_2 \quad (A\ {}^3\Sigma_u^+)$$

The following reactions may also be involved.

$$NO + h\nu\ (\text{Lyman } \alpha) \rightarrow NO^+ + e^-$$

$$NO + h\nu \xrightarrow{1900\ A} N + O$$

Lyman alpha through predissociation is able to dissociate nitrogen.

$$N_2 + h\nu \rightarrow N + N$$

At twilight nitrogen atoms may be produced by the dissociative recombination

$$NO^+ + e^- \rightarrow N + O$$

Bates, D.R. and M.R.C. McDowell, "Recombination in the Ionosphere During an Eclipse", J. Atmos. Terrest. Phys., 10, 96-102, (1957).

In this mathematical treatment of recombination in the ionosphere, the authors briefly mention recombination mechanisms thought to be operative in the E and F regions. In particular reference is made to the processes by which atomic ions are converted into molecular ions by charge transfer

$$O^+ + O_2 \rightarrow O + O_2^+$$

and by ion-atom transfer

$$O^+ + O_2 \rightarrow O_2^+ + O$$

$$O^+ + N_2 \rightarrow NO^+ + O$$

and also to the mechanism in which free charges are removed by dissociative recombination.

$$O_2^+ + e^- \rightarrow O' + O''$$

$$NO^+ + e^- \rightarrow N' + O'$$

$$N_2^+ + e^- \rightarrow N' + N''$$

Broida, Herbert P. and Donald F. Heath, "Luminous Reaction Between Carbon Monoxide and Atomic Nitrogen", J. Chem. Phys., 26, 1352, (1957).

The authors report that the reaction between CO and atomic nitrogen at pressures of about 3 mm Hg was observed to give a fairly bright violet and orange glow. The spectra from that reaction were predominantly the red and violet systems of CN. Also, under some conditions the first positive system of N_2 was present. The spectra from atomic nitrogen and acetylene under the same conditions as those

for CO and atomic nitrogen showed the CN bands to have nearly the same intensity and intensity distribution as for CO and atomic nitrogen.

Broida, Herbert P. and Maurice Peyron, "Luminescence of Solid Nitrogen (4.2°K) Containing Atoms or Free Radicals. Effect of Dilution with Argon", J. Phys. radium, 18, 593-595, (1957).

The experimental procedure is briefly described. The microwave discharge technique was employed. The study was concerned with both pure solid nitrogen and mixtures of solid argon and nitrogen. The solids were rapidly frozen on a glass surface at liquid helium temperature. The authors state that metastable atoms are probably trapped in the solid and are able to radiate. Some observed molecular spectra are probably formed by recombination. New band systems were observed when the nitrogen was diluted with argon and some of the lines were shifted.

Bryan, R. B., R. B. Holt, and O. Oldenberg, "Recombination and Afterglow in Nitrogen and Oxygen", Phys. Rev., 106, 83-86, (1957).

This paper reports the measurement of the coefficient of electron recombination α of nitrogen at a pressure of 3 to 30 mm Hg by the microwave cavity technique. Spectrograms were obtained. It is significant that no permitted or forbidden lines observed in the spectra could be ascribed to atomic nitrogen.

If the recombination ($N_2^+ + e$) occurred by dissociative recombination ($N_2^+ + e^- \rightarrow N^{1} + N^{1}$) it would not depend on the pressure. Actually it was found that the rate increases with the pressure, which was taken to indicate a contribution of triple collisions.

The explanation is based upon the assumption that two active particles forming a molecule consist of normal and metastable atoms, the metastable ones survived from the discharge, whereas a triple collision

may lead to the formation of excited N_2 molecules.

Carleton, N. P., "Excitation of Nitrogen by Protons of a Few Kev Energy", Phys. Rev., 107, 110-113, (1957).

The purpose of this study was to aid in interpreting auroral spectra. Protons were generated in an rf-discharge ion source described by Moak, Reese, and Good [Nucleonics, 9, No. 3, 18, (1951)]. A schematic diagram of the apparatus is included in the paper.

With reference to atomic nitrogen, the author considers the N I lines to be produced by a simple collision process.

$$H^+ + N_2 \rightarrow N + N' + H^+$$

This reaction requires that $\Delta E = 21.5$ ev, which would not be favored at low bombarding energies. Reference is made to Massey and Burhop [p. 263, Electronic and Ionic Impact Phenomena, Clarendon Press, Oxford, (1952)] who state that there is no known process through which a nitrogen molecule may be dissociated into two neutral atoms by electron impact. However, the author of the present paper states that there is not conclusive evidence for this. Unpublished work by Balls and Carleton give evidence from experiments on absorption of nitrogen activated by electron bombardment which indicates that such a process may exist.

Cole, T., John T. Harding, John R. Pellam, and Don M. Yost, "EPR Spectrum of Solid Nitrogen Afterglow at $4.2^\circ K$", J. Chem. Phys., 27, 593-594, (1957).

Because the Rayleigh afterglow induced in nitrogen is of importance in studies of the earth's atmosphere and also in chemistry, physics, and astrophysics, this study of an electron paramagnetic resonance (EPR)

spectrum of thermally condensed activated nitrogen was undertaken.

The afterglow described in the present paper was produced from a flow of nitrogen gas at about 1 mm Hg pressure through a microwave resonator attached to a 2450-Mc Rayehton diathermy unit. The pressure was adjusted to obtain the familiar yellow afterglow of nitrogen. The glowing gas was then condensed at $4.2^{o}K$ in the form of a glowing solid.

Figure 1 in the paper shows an electron paramagnetic (EPR) spectrum of atomic nitrogen condensed at $4.2^{o}K$. The authors explain that atomic nitrogen in its ground state is represented electronically by $1s^2\ 2s^2\ 2p^3\ {}^4S_{3/2}$. The total electronic spin is $S = 3/2$ and the nuclear spin of $I = 1$. Three distinct lines are shown with splitting from the central line of $4.5 \pm 0.4 \times 10^{-4}$ weber/m^2.

Dufay, Maurice, "Le spectre d'une aurorae le basse latitude dans le visible et le proche infrarouge", "Spectrum of a low-latitude aurora in the visible and near infrared", Compt. rend., 245, 1648-1650, (1957).

The observation reported by Dufay was made at the observatory of Haute-Provence during an aurora occurring on the night of 29-30 September 1957. The doublet ${}^4S - {}^2D$ of N I was present with exceptional intensity.

Glick, H.S., J.J. Klein, and W. Squire, "Single-Pulse Shock Tube Studies of the Kinetics of the Reaction $N_2 + O_2 \rightarrow 2NO$ Between 2000-3000^{o}K", J. Chem. Phys., 27, 850-857, (1957).

The method of study given in this report was developed at the Cornell Aeronautical Laboratory, Inc., Buffalo, New York. The single-pulse shock tube technique is discussed and a diagram of the shock tube is included. Other topics discussed under data analysis are reaction temperature calculation, data reduction, experimental results, and discussion of results.

The chain mechanism proposed by Zeldovich [Acta Physicochim, U.R.S.S., 21, 577, (1946)] was found to be consistent with the kinetics of the reaction,

$$M + 1/2\, O_2 \rightleftharpoons M + O$$

$O + N_2 \rightleftharpoons NO + N,$ $\Delta H_{2500^o} = +75.8$ kcal/mole

$N + O_2 \rightleftharpoons NO + O,$ $\Delta H_{2500^o} = -32.5$ kcal/mole

with an over-all reaction

$N_2 + O_2 \rightleftharpoons 2NO.$ $\Delta H_{2500^o} = 43.2$ kcal/mole

Harteck, P., "A Discussion of the Reactions of Nitrogen and Nitrogen Oxides in the Upper Atmosphere", The Threshold of Space, The Proceedings of the Conference on Chemical Aeronomy held at Cambridge, Massachusetts, 25-28 June 1956, edited by M. Zelikoff, pp 32-39, Pergammon Press, N.Y., London, (1957).

This paper is concerned primarily with reactions which may occur at an altitude of 90 - 110 km or higher. Above this altitude range molecular oxygen is to a large extent dissociated into atoms due to the absorption of ultraviolet radiation in the region λλ 1760 to 1300 A. Knowing only the dissociation of oxygen, our understanding of the many reactions between atomic and molecular oxygen and nitrogen and nitrogen oxides is very limited.

Reference is made to the observations of Professor Groth who showed that nitrous oxide (N_2O) can decompose into molecular nitrogen and an oxygen atom and also into atomic nitrogen and nitric oxide. Thus in two steps, (a) the formation of nitrous oxide and (b) the decomposition of N_2O, nitrogen may be decomposed without requiring a wavelength shorter

than 1300 A. However this process should be regarded only as a minor contribution to the dissociation of molecular nitrogen.

The author states that according to the literature, about 10^9 - 10^{10} nitrogen atoms/cm^2 sec are formed by ultraviolet radiation, while 2×10^{12} oxygen atoms/cm^2 sec are formed. Reference is made to the use of cobalt-60 as a source for quantitative experiments in radiation chemistry.

In Table 1 Harteck lists most of the reactions involved in the nitrogen-oxygen system. These reactions are reproduced here together with the column Log K at $300^\circ K$, the rate constant in particle concentration, cm^3/sec for bimolecular reactions and cm^6/sec for trimolecular reactions. Reactions (3), (4), (8a, b, c,) (9), and (12) are included in Table 2 as being those of especial pertinence to the upper atmosphere.

No.	Reaction	Log K at $300^\circ K$
1a	$N_2 \longrightarrow N^+ + e^-$	
1b	$N_2 \longrightarrow N_2^*$	
$1c_1$	$N_2^* \longrightarrow N + N$	
$1c_2$	$N_2^+ + e^- \longrightarrow N + N$	
2a	$O_2 \longrightarrow O_2^+ + e^-$	
2b	$O_2 \longrightarrow O_2^*$	
$2c_1$	$O_2^* \longrightarrow O + O$	
$2c_2$	$O_2^+ + e^- \longrightarrow O + O$	
3	$N + O_2 \longrightarrow NO + O$	$-16\ cm^{-3}$
4	$NO_2 + O \longrightarrow NO + O_2$	$-15\ cm^{-3}$

No	Reaction	Log K at 300°K
5	$2\,NO + O_2 \rightarrow 2\,NO_2$	$-37\ cm^{-6}$
6	$2\,NO_2 \rightleftharpoons N_2O_4$	
7a	$NO_2 \rightarrow NO_2^+ + e^-$	
7b	$NO_2 \rightarrow NO_2^*$	
$7c_1$	$NO_2^* \rightarrow NO + O$	
$7c_2$	$NO_2^+ + e^- \rightarrow NO + O$	
$7d_1$	$NO_2^* \rightarrow N + 2\,O$	
$7d_2$	$NO_2^+ + e^- \rightarrow N + 2\,O$	
8a	$NO_2 + N \rightarrow 2\,NO$	$-14.3\ cm^{-3}$
8b	$NO_2 + N \rightarrow N_2O + O$	$-14.5\ cm^{-3}$
8c	$NO_2 + N \rightarrow N_2 + 2\,O$	$-14.7\ cm^{-3}$
9	$NO + N \rightarrow N_2 + O$	$-13\ cm^{-3}$
10a	$N_2O \rightarrow N_2O^+ + e^-$	
10b	$N_2O \rightarrow N_2O^*$	
$10c_1$	$N_2O^* \rightarrow N_2 + O$	
$10c_2$	$N_2O^+ + e^- \rightarrow N_2 + O$	
$10d_1$	$N_2O^* \rightarrow NO + O$	
$10d_2$	$N_2O^+ + e^- \rightarrow NO + O$	
$10e_1$	$N_2O^* \rightarrow 2N + O$	
$10e_2$	$N_2O^+ + e^- \rightarrow 2N + O$	

No.	Reaction	Log K at 300°K
11a	$NO \longrightarrow NO^{+} + e^{-}$	
11b	$NO \longrightarrow NO^{*}$	
$11c_1$	$NO^{*} \longrightarrow N + O$	
$11c_2$	$NO^{+} + e^{-} \longrightarrow N + O$	
11d	$NO + M^{+} \longrightarrow NO^{+} + M$	-12
12	$NO + O \longrightarrow NO_2 + h\nu$	-15
13a	$O + O + M \longrightarrow O_2 + M$	-32.7
13b	$O + O \longrightarrow O_2 + h\nu$	
14a	$N + N + M \longrightarrow N_2 + M$	
14b	$N + N \longrightarrow N_2 + h\nu$	
15a	$N + O + M \longrightarrow NO + M$	-32.7
15b	$N + O \longrightarrow NO + h\nu$	
16a	$N_2 + O + M \longrightarrow N_2O + M$	-41 cm^{-6}
16b	$N_2 + O \longrightarrow N_2O + h\nu$	-30
16c	$N_2O \longrightarrow N_2 + O$	-00
17	$N_2 + O_3 \longrightarrow N_2O + O_2$	33

Reference is made to the recombination coefficient for reaction (12) in Table 1.

(12) $NO + O \longrightarrow NO_2 + h\nu$

Gaydon's considerations appear to confirm a value of 10^{-15} rather than 10^{-17} for this reaction. A list of conclusions is given by combining the number density of atomic oxygen and atomic nitrogen at an altitude of about 105 km with reactions (3), (4), (8a, b, c,), and (12).

Harteck, P. and S. Dondes, "Decomposition of Nitric Oxide and Nitrogen Dioxide by the Impact of Fission Fragments of Uranium-235", J. Chem. Phys., 27, 546-551, (1957).

This is an excellent paper describing the experimental methods, reactants, and reaction products and giving a full discussion of the results obtained. Table 1 gives an extensive list of important chemical equations concerning the mechanism of the reactions. The table is an excerpt of the table included in the abstract of the paper by Harteck presented at the symposium on chemical aeronomy and published in Treshold of Space.

With reference to the decomposition of nitric oxide yielding nitrous oxide (N_2O) according to the following mechanisms

(a) $NO + N = N_2O + h\nu$

(b) $NO + N + M = N_2O + M$

the authors state that during the first 10 minutes of the decomposition of NO, no N_2O formation was observed. They concluded that nitric oxide could only be decomposed by nitrogen atoms according to the following mechanism

$$NO + N \longrightarrow N_2 + O$$

The nitrogen atoms could be produced from both nitric oxide decomposition and from the associated decomposition of molecular nitrogen, nitrous oxide, and nitrogen dioxide. From the table of reaction mechanisms the authors point out that nitrogen dioxide (NO_2) is "autocatalytically decomposed by its own products".

Hepner, G. and L. Herman, "Spectrum of Nitrogen between 0.9 and 2.6 μ", Ann. geophys., 13, 242-248, (1957).

The spectra were obtained by a discharge tube containing helium at a pressure of 3 mm Hg and N_2 at 0.1 mm Hg pressure. The radiations were recorded with a PbS detector. In the spectral region from 1.06 to 1.13 μ six lines of N I belonging to the transitions 3p $^4D^0 \rightarrow$ 4s ^4P and 3p $^4P^0 \rightarrow$ 3d $^4P^0$ were measured. Other bands belonging to the system B $^3\Pi$ - A $^3\Sigma_u^+$ were measured in the spectral range 1.15 to 2.54 μ. In the region from 2.3 to 2.6 μ a new system of four bands was discovered. This new system was considered to be due probably to the $^5\Pi \rightarrow {}^5\Sigma$ transition. A bibliography of ten references is included in the paper.

Herzfeld, C. M., "Theory of the Forbidden Transitions of Nitrogen Atoms Trapped in Solids", Phys. Rev., 107, 1239-1245, (1957).

A detailed theory is given of the forbidden transitions of nitrogen atoms trapped in solids. In a previous paper the author and Broida [Phys. Rev., 101, 606, (1956)] had assumed (a) that some of the trapped nitrogen atoms were deposited while in the excited $2p^3\ {}^2D$ state going by a radiative process to the ground state $2p^3\ {}^4S$, and (b) that recombination of atoms produced excited N_2 molecules in the $^5\Sigma$ state which went to the $^3\Sigma$ state by a radiative transition.

In the present paper the author has reported a detailed examination of the perturbing effects of neighboring molecules on the transition $2p^3\ {}^2D \rightarrow 2p^3\ {}^4S$. The formal theory involves the calculation of the quantum mechanical averages of the effects of V on the states $2p^3\ {}^2P$, $2p^3\ {}^2D$, and $2p^3\ {}^4S$, taking configuration interaction with $2p^2\ {}^3s$ and $2p^2\ {}^3p$ into account. The symbol V describes the perturbation of the electrons of the nitrogen atom by the neighboring molecules and depends upon the arrangements of these neighboring molecules

In the theory which is presented the author has shown that configuration interaction is important. Splittings and shifts of levels and reduction of half-lives are explained. The trapping sites of atoms are shown to have low symmetry and to be nearly identical for different atoms. The theory and calculations confirm the presence of nitrogen atoms in the low-temperature deposits from electric discharges.

Johnson, C.Y., J.C. Holmes, and E. B. Meadows, "Ion Composition of the Ionosphere at Fort Churchill, Canada, by Rocket-Borne Spectrometers", Trans. Am. Geophys. Union, 38, 397, (1957).

During the flight following the rocket launching at Fort Churchill, Canada, 20 November 1956, two minor positive ions of mass 28 and 18 were detected. These were identified as 28-N_2^+ and 18-H_2O^+. Other positive ions in greater abundance were 32 - O_2^+, 30=NO^+, and 16-O^+. The mass-16 positive ion predominated with increasing altitude.

Kaufman, Frederick and John R. Kelso, "Excitation of Nitric Oxide by Active Nitrogen", J. Chem. Phys., 27, 1209-1210, (1957).

The authors have studied the nitrogen afterglow and the composition of active nitrogen by adding $N^{14}O$ and $N^{15}O$ to a stream of active nitrogen. Reference is made to recent mass-spectrometer studies which suggest as a reasonable explanation of the origin of the nitrogen afterglow that the phenomenon is due to ground-state ^4S nitrogen atoms as the major constituent. The long-known phenomenon of color change produced by the addition of a small quantity of nitric oxide to active nitrogen is reviewed. The change is from orange yellow through pink and purplish blue to colorless and then to the greenish-yellow air afterglow, when increasing amounts of nitric oxide are added to active nitrogen. Reference is also made to the experiments of Tanaka [J. Chem. Phys., 22, 2045, (1954)]

who demonstrated that the NO-β and γ - band systems were strongly emitted in the pink and blue stages.

The authors report that if the added nitric oxide is raised to the $A\ ^2\Sigma$ and $B\ ^2\Pi$ states from which the B and X systems are emitted one can observe that the pink or blue color is present immediately at the point of mixing active nitrogen with nitric oxide and also persists over a long distance in a moderately fast flow system. The addition of a somewhat larger quantity of nitric oxide completely extinguishes the glow.

In order to account for the presence of nitric oxide and active nitrogen over a considerable period of time it is pointed out that the following very rapid reaction

(a) $\quad NO + N \longrightarrow N_2 + O$

proceeds with the complete distruction of NO as long as active nitrogen is in excess.

The following mechanism

(b) $\quad N + O \xrightarrow{(+M)} NO^* \longrightarrow NO + h\nu$

could account for the NO emission.

The present investigation was an attempt to decide which explanation is correct. Experimental details are fully described. $N^{14}O$ and $N^{15}O$ were added to active nitrogen. The NO- emission spectra were observed employing a Leeds and Northrup recording grating spectrometer. Active nitrogen was obtained by means of an electrodelss microwave discharge of 2400-mc frequency and about 50 to 100-w microwave power output (Raytheon Microtherm Model CMD-4).

The principal conclusion reached in this investigation was that NO is not excited by active nitrogen but rather is rapidly decomposed. It appeared that the NO added downstream from the discharge weakens the Lewis-Rayleigh afterglow by reaction (a) and produces NO according to reaction when there is an excess of active nitrogen. This accounts for the range of glows from yellow to blue. In the blue state only a little atomic nitrogen is present while much atomic oxygen is produced. Nitric oxide (NO) added in slight excess depletes the atomic nitrogen causing both the NO* bands and the glow to disappear. A further addition of NO produces the greenish-yellow NO - O continuum since there are high concentrations of both atomic oxygen and nitric oxide existing together.

Kistiakowsky, G. B., and G. G. Volpi, "Reactions of Nitrogen Atoms. I. Oxygen and the Oxides of Nitrogen", J. Chem. Phys., 27, 1141-1149, (1957).

The authors state in the introduction that besides N_2 molecules in the normal state the only constituent of measurable concentration in active nitrogen is atomic nitrogen in the normal ^4S electronic state. As evidence for this the following references are given: D.S. Jackson and H. I. Schiff, J. Chem. Phys., 23, 2333, (1955); and Berkowitz, Chupka, and Kistiakowsky, J. Chem. Phys., 25, 457, (1956).

In the present paper several reactions of nitrogen atoms were studied in a low-pressure flow system. A mass spectrometer was employed to determine the steady-state concentrations. The experimental details are fully described.

Reaction with Nitric Oxide (NO)

$N + NO = N_2 + O \quad k_1 \geq 4 \times 10^{11}\ \text{cc mole}^{-1}\ \text{sec}^{-1}$

$O\ (+\ \text{wall}) = 1/2\ O_2\ (+\ \text{wall})$

$O + NO = NO_2^*$

$NO_2^* + M = NO_2 + M$

$NO_2^* = NO + O$

$O + NO_2 = NO + O_2$

$NO_2^* = NO_2 + h\nu$

Reaction with Oxygen, O_2

$N + O_2 = NO + O \quad k_8 = 2 \times 10^{12} \exp(-6200/RT)\ \text{cc mole}^{-1}\ \text{sec}^{-1}$

Mechanism

$N + O_2 = NO + O$

$N + NO = N_2 + O$

$O\ (+\ \text{wall}) = 1/2\ O_2\ (+\ \text{wall})$

Reaction with Nitrous Oxide

The reaction

$N\ (^4S) + N_2O\ (^1\Sigma) = N_2\ (^1\Sigma) + NO\ (^2\Pi)$

is forbidden by the rule of conservation of spin. No reaction was noted between nitrogen atoms and nitrous oxide in the temperature range from 25 to 280^o. Reference is made to the paper by Zelikoff and Aschenbrand [J. Chem. Phys., 22, 1680, (1954)].

Reaction with Nitrogen Dioxide, NO_2

$N + NO_2 = N_2O + O \quad 10^{-2}\ K_1 < K_9 < 10\ K_1$

$N + NO_2 = N_2O + O$ (10)

$O + NO_2 = N\ O + O_2$ (6)

$N + NO = N_2 + O$ (1)

$O\ (+wall) = 1/2\ O_2 + (wall)$

$O + NO = NO_2 \quad K_3 \geq 10^{13}$ cc mole^{-1} sec^{-1}

$O + NO_2 = O_2 + NO \quad K_6 \geq 10^{12}$ cc mole^{-1} sec^{-1}

The rate constants are at room temperature. The authors state that the observations on the nitrogen atom - nitrogen dioxide systems demonstrate the existence of two mechanisms for the formation of nitrous oxide when free atoms are present. Harteck and Dondes [J. Chem. Phys., 24, 619, (1956)] did not consider this reaction in the formation of atmospheric nitrous oxide in the upper atmosphere.

$N + NO_2 = 2\ NO$

$N + NO_2 = N_2 + O_2$

$O + NO_2 = NO^* + O_2$

$NO^* + NO_2 = N_2O + O_2$

Kistiakowsky, G. B. and Peter Warneck, "Lewis-Rayleigh Nitrogen Afterglow", J. Chem. Phys., 27, 1417-1418, (1957).

This is a report of the measurement of the band intensities (5300 to 10600 A) in the afterglow of N_2^{14} and 99.7% pure N_2^{15} with a resolution of about 10 A at temperatures of 100, 200, and 300°K. Dilutants were He, Ne, A, and Kr.

Figure 1 in the paper shows a shift in the normalized population distribution of N_2^{14} and N_2^{15} from a peak at about 1900 cm^{-1} to lower energies with rising temperature. When extrapolated to 0°K, its position was found to coincide with the energy of the $^5\Sigma_g^+$ state.

This was taken to be proof of a two-step mechanism for the afterglow.

$$N + N + M \rightleftharpoons N_2\ ({}^5\Sigma_g^+) + M \rightarrow N_2({}^3\Pi_g) + M$$

Kurzweg, U.H., A.M Bass, and H.P. Broida, "Spectra of Afterglows and Discharges from Nitrogen-Oxygen Mixtures", J. Molec. Spectroscopy, 1, 184-200, (1957).

This is an excellent summary and systematic investigation of the spectra of the afterglows in mixtures of nitrogen and oxygen. Reference is made to the surveys on this subject by Mitra [Active Nitrogen - A New Theory, Indian Association for the Cultivation of Science, Calcutta, (1945)] and Glocker and Lind [The Electrochemistry of Gases and Other Dielectrics, Chap. XII, p. 255 ff, John Wiley and Sons, Inc., New York, (1939)]. The apparatus is described in detail including the discharge system, spectrographs and optical alignment, and gases and flowmeter. Other topics fully described are (a) the experimental procedure, (b) experimental results, (c) visual appearance of the afterglows, (d) the tube effect, (e) pressure effect, (f) flow effect, and (g) other effects. Four excellent photographs of spectrograms fully labeled and explained are included and enhance the value of this study.

Lichten, William, "Lifetime Measurements of Metastable States in Molecular Nitrogen", J. Chem. Phys., 26, 306-311, (1957).

The lifetimes of two metastable states of molecular nitrogen, a ${}^1\Pi_g$ and A ${}^3\Sigma_u^+$, were determined. Both states are known to decay to the ground state X ${}^1\Sigma_g^+$ by emitting radiation forbidden

by the electric dipole selection rules. It is stated that the Lyman-Birge-Hopfield bands result from the magnetic dipole transition a $^1\Pi_g \longleftrightarrow X\ ^1\Sigma_g^+$, and the Vegard-Kaplan system results from the electric dipole intercombination transition A $^3\Sigma_u^+ \rightarrow X\ ^1\Sigma_g^+$.

The essential features of the apparatus and instrumentation are described and the results are discussed in detail. A lower limit of 10^{-2} sec was obtained for the lifetime of the A $^3\Sigma_u^+$ state and the measured lifetime of the a $^1\Pi_g$ state of N_2 was found to be 1.7 ± 0.3 sec.

Lofthus, Alf., "Emission Band Spectra of Nitrogen. A Study of Some Singlet Systems", Can. J. Phys., 35, 216-234, (1957).

This is a contribution from the Department of Physics, University of Oslo, Blindern, Norway. The research was supported by the Norwegian Research Council of Science and the Humanities. Ten bands of Gaydon's and Herman's singlet systems and 8 new bands were photographed under high resolution and analyzed in detail. Two of the new transitions were shown to be $^1\Sigma_u^+ \rightarrow a\ ^1\Pi_g$. It is proposed that the new state $^1\Delta_g$ has the same electron configuration as the x $^1\Sigma_u^+$ state.

Identification of the electronic structure of the higher singlet states in terms of Rydberg orbitals is discussed.

Lofthus, Alf and Robert S. Mulliken, "Emission Band Spectra of Nitrogen, Kaplan's First and Second Systems", J. Chem. Phys., 26, 1010-1017, (1957).

The work reported in this paper was in part supported by the Geophysics Research Directorate of the Air Force Cambridge Research Center, Air Research and Development Command. The authors photographed seven bands of Kaplan's first system and eleven bands of Kaplan's second system.

Photographs are shown and analyses of lines in wave numbers are given in tables. Interpretations of the states π_u^3 and $2\pi_g$ of N_2, and the X and Y states of N_2 are thoroughly considered in the discussion.

Nicolet, Marcel, "Nitrogen Oxides and the Airglow", The Threshold of Space, pp. 40-57, Pergamon Press, New York, London, (1957).

In this discussion of the aeronomic problem of nitrogen oxides it is pointed out that the behavior of nitrogen oxides is dependent upon the dissociation of molecular nitrogen. The vertical distribution of nitrogen atoms in the mesophere and thermosphere is determined by mixing and/or diffusion instead of local equilibrium.

Atomic nitrogen enters into the formation of nitric oxide due to a three-body collision process $N + 0 + M \xrightarrow{b_1} NO + M$

The rate coefficient, b_1 is adoped to be $b_1 = 5 \times 10^{-34} \ T^{1/2} \ n\,(M)$.

In the photodissociation of NO, $NO + h\nu \xrightarrow{J_{NO}} N + O$ for which according to Bates [Am. Geophys., 8, 194, (1952)] the rate coefficient J_{NO} is $J_{NO} = 10^{7} \sec^{-1}$.

For the reaction $N + NO \xrightarrow{b_8} N_2 + O$ accounting for the disappearance NO, Nicolet [J. Atmos. Terrest. Phys., 7, 152, 297, (1955)] has adopted the coefficient $b_8 = 1.5 \times 10^{-14} T^{1/2} e^{-2.9/RT}$, giving a value of 2×10^{-15} at 300°K. From further reasoning Nicolet arrives at the mean lifetime of a nitrogen atom to be 1.5×10^5 sec. at 50 km and 1.3×10^6 sec. at 75 km.

From theoretical considerations of the airglow, the formation of nitric oxide, and the Vegard-Kaplan band system the number density of nitrogen atoms was deduced to be

$n(N) = 2 \times 10^6 \text{ cm}^{-3}$ at 50 km and $n(N) = 2 \times 10^7 \text{ cm}^{-3}$ at 80 km

The author states that detection of the Vegard-Kaplan bands in the airglow spectra requires that n(N) should not be less than 10^8 cm^{-3}.

Oldenberg, O., "The $^5\Sigma$ Level of the Nitrogen Molecule", The Threshold of Science, pp. 180-185, Pergammon Press, New York, London, (1957).

Reference is made to a band system in active nitrogen observed by Broida and Pellam [Phys. Rev., 95, 845, (1954)]. The active nitrogen was obtained by activation of molecular nitrogen by an electric discharge and was subsequently frozen at liquid helium temperature. The band system was interpreted as a $^5\Sigma \rightarrow {}^3\Sigma$ transition.

In the present paper Professor Oldenberg discusses the $^5\Sigma$ level as perturbing other levels.

Robinson, Lawrence Baylor, "Elastic Scattering of Low-Energy Electrons by Atomic Nitrogen and Atomic Oxygen", Phys. Rev., 105, 922-927, (1957).

The author points out that an understanding of the various processes occurring in the upper atmosphere involves the scattering of low-energy electrons by atomic nitrogen and atomic oxygen. The phase shifts and elastic scattering cross sections of atomic nitrogen and oxygen for low energy electrons are calculated with central field potentials with most emphasis on the Hartree-Fock potentials. The detailed mathematical formulation is given. The Thomas-Fermi potential in equation (22) of the paper was shown to allow for the existence of a bound state, of approximately zero energy, in the case of atomic oxygen.

Schram, H., R.W. Lunt, and L. Herman, "Influence of Electronic and Molecular Concentration on the Apparent Probability of the $A\ ^3\Sigma_u - X\ ^1\Sigma_g$ Transition in the Nitrogen Molecule", J. Phys. radium, 18, 59-67, (1957).

The authors state that deactivation by collision is essential in the equilibrium existing between different constituents in gaseous nebulas and ionized layers of the upper atmosphere. The purpose of the experiment reported here was to isolate the effects of deactivation by electronic and molecular collisions for pure nitrogen and nitrogen-xenon mixtures. The mean energy of the electrons was determined by a two-probe system with the gases contained in a discharge tube. The electronic concentration was calculated; it varied with the discharge current. The radiation intensity of the

2nd positive system $C\ ^2\Pi$ - $B\ ^3\Pi$ and of the intercombination system $A\ ^3\Sigma$ = $X\ ^1\Sigma$ of nitrogen was measured as a function of the electronic concentration in the positive column. These data permitted an estimate to be made of the electronic and molecular deactivation coefficients.

Semenov, S.S., "Method of Checking the Equation of State for Gases at High Temperatures", Doklady Akad. Nauk, S.S.S.R., 114, 840-843, (1957).

The author has derived the ratio of densities in front of and behind a shock wave from measurement of the shock wave angle. The energy of dissociation of molecular nitrogen was determined and shown to have the value $D(N_2)$ = 9.76 ev.

Tanaka, Y., A. Jursa, and F. LeBlanc, "Vacuum Ultraviolet Spectra of the Afterglows of Pure N_2 and a Mixture of N_2 and O_2", The Threshold of Space, pp. 89-93, Pergammon Press, London, (1957).

Brief mention is made of the four different stages of the nitrogen afterglow. They are different from one another in their color and in their emission spectra. Figure 1 in the paper gives a comprehensive summary of the emission and absorption spectra observed in the four stages of the afterglow. The first stage (straw-yellow) is the well known Lewis-Rayleigh afterglow which is produced in extremely pure N_2. In the present study the authors report that in addition to the first positive bands of N_2, they observed the $a\ ^1\Pi_g$ - $X\ ^1\Sigma_g^+$ bands of emission in the vacuum region. These

are shown in Table 2.

The absorption spectrum of this first stage in the vacuum region showed four groups of N I lines which are listed in Table 1. The concentration of $N(^4S)$ in the glow was about 0.1 percent of the total pressure of N_2, and that of both $N(^2D)$ and $N(^2p)$ approximately 500 times less than that of $N(^4S)$. This appeared to verify the existence of a large amount of $N(^4S)$ in the afterglow which had previously been suggested by Cario and Reinecke (1949).

There is no sharp boundary between the [second stage (blue)] and the first stage. This stage (characterized by strong NO bands,) occurs when only a slight impurity of O_2 exists. When the amount of O_2 was increased the glow color became pure blue while the first positive bands completely disappeared. The absorption spectrum in the vacuum region showed both strong N I and O I lines. The NO molecule was not detected in the absorption; however it was observed in the emission spectrum indicating the presence of NO in the glow.

In the third stage (dark) the O I lines and some unidentified bands were observed.

It is suggested that as the O_2 pressure increased the concentration of $N(^4S)$ decreased, while that of $O(^3p)$ and NO $(X\ ^2\Pi)$ increased.

In the fourth stage (greenish gray) the emission spectrum was identical with the so-called air afterglow described by Tanaka and Shimazu [J. Sci. Res. Institute, (Tokyo), 43, 241, (1949)].

The existence of $O(^3p)$ and $NO(X\ ^2\Pi)$ was confirmed in the absorption spectrum. The authors remark that the absorption bands appeared as soon as a slight amount of O_2 was added to the pure N_2. These bands persisted throughout the remaining stages, the intensity increasing with increased pressure of O_2.

Toennies, J.P. and E.F. Greene, "Dissociation Energies of Carbon Monoxide and Nitrogen from Reflected Shock Wave Studies", J. Chem. Phys., 26, 655-662, (1957).

The authors state that only recently has some agreement been reached about dissociation of molecular nitrogen. The results from spectroscopic, thermal, electron impact, and shock and detonation experiments are in agreement on favoring the so-called high value for $D(N_2) = 9.76$ ev or 225 Kcal $mole^{-1}$.

The method, apparatus, and experimental procedure are described in detail. The results obtained are discussed under the headings dissociation energies, measurement on mixtures of the gases with argon, relaxation, and attenuation. The results for both the pure gases and dilute mixtures in argon, the latter being a relatively new case, were considered to provide new evidence for the value for $D(N_2) = 225$ Kcal $mole^{-1}$ or 9.76 ev, and $D(CO) = 256$ Kcal $mole^{-1}$ or 11.1 ev.

1958

Akriche, J. and L. Herman, "Emission Moleculaire et Recombinaison Atomique Dans L'Azote", J. Phys. radium, 19, 649-657, (1958).

Calculations are made for the distribution of the population of different vibrational levels of an excited diatomic molecule formed by the collision of two atoms. The calculations are compared with experimental results obtained from the afterglow of the first positive system of nitrogen emitted in a mixture of nitrogen and helium.

The conclusion is reached that the molecules of nitrogen are ionized in the presence of metastable helium atoms.

Barbier, Daniel, "Auroral Activity at Low Latitudes", Ann. geophys, 14, 334-355, (1958).

The results and observations of auroral activity at low latitudes are fully described. The observations were made at the Observatory of Haute-Provence, latitude 43.9°N. The forbidden N I line at 5200 A was frequently observed. Many photometric measurements were made.

Bayes, K.D. and G.B. Kistiakowsky, "On the Mechanism of the Lewis-Rayleigh Nitrogen Afterglow", J. Chem. Phys., 29, 949-950, (1958).

This paper reports the continuation of measurements of the band intensities in the first positive and the new Y system using N_2^{14} and N_2^{15}. The authors make reference to the experiments of LeBlanc, Tanaka, and Jursa [J. Chem. Phys., 28, 979, (1958)] who accurately measured frequencies of many band heads in the new Y system. The transition was interpreted as $^3\Delta_u \rightarrow B\ ^3\Pi_g$.

This interpretation is discussed with reference to frequency in intensity measurements.

Bialecke, E.P. and A.A. Dougal, "Pressure and Temperature Variation of the Electron-Ion Recombination Coefficient in Nitrogen", J. Geophys. Res., 63, 539-546, (1958).

This paper gives the results of the measurement of the electron-ion recombination coefficient α_{ei} in ionized nitrogen gas. The pressure range was 0.2 to 2 mm Hg and the electron temperature range was 92 to 300^{o}K. The electron-ion recombination coefficient α_{ei} varied from 6.7×10^{-6} cm^{3}/sec at 92^{o}K to 8.7×10^{-6} cm^{3}/sec at 300^{o}K and a pressure of 1.3 mm Hg.

Among the recombination mechanisms in the ionized molecular nitrogen gas the dissociative recombination

$$N_2^+ + e^- \rightarrow N^* + N^*$$

appeared to have the highest probability. This study was taken to support the dissociative recombination theory of Bates and Mitra, working independently as the source of atomic nitrogen in the upper atmosphere.

Borisoglebskii, L.A., "Forbidden Lines in Atomic Spectra", Uspekhi Fiz. Nauk, 66, 605-652, (1958).

This is a comprehensive review and survey of forbidden lines in atomic spectra. Of interest to geophysics of the upper atmosphere, the lines of atomic nitrogen and atomic oxygen are discussed. Figure 4 in the paper is a diagram transition for

the forbidden lines λλ3466.5, 10,405, 5200.1, and 5197.8 A of N I.

A total of 166 references are included in the bibliography. Those pertaining to atomic nitrogen are the following: Pasternack [Astrophys. J., 92, 129, (1940)]; Ufford and Gilmour [Astrophys. J., 111, 580, (1950)]; and Nicolet [Naturwiss., 51, 839, (1938)].

Broida, H.P., "Trapped Radicals", Endeavour, 17, 208-215, (1958).

A free radical is defined to be a chemical fragment, either atomic or molecular, which has an unpaired electron spin. The reactivity of the radical is attributed to the unpaired electron. A brief historical background of free radical study is given which is divided roughly into three periods. The first stage began with the observation of Dewar [Proc. Roy. Soc., 68, 360, (1901)] and includes the work of R.J. Strutt (later, Lord Rayleigh), the studies of McLennan at Toronto, Canada, and the investigations of Lars Vegard, who employed low temperature techniques down to 4.2°K.

The second stage includes the studies of reactions of radicals on cold surfaces and involved the development of chain mechanisms. A list is given of a number of those whose research work was in this field. The third and current stage involving new techniques of modern technology began in the early 1950s with the work of F.O. Rice. The development of such physical methods as electron spin resonance, magnetic susceptibility, optical spectroscopy, and mass spectroscopy in the study of trapped radicals has greatly accelerated this current phase.

A detailed account of experimental technique is given. Two full pages of 16 color photographs of the afterglow of active nitrogen greatly enhances the attractiveness of this paper. Dr. Broida concludes this paper with a discussion of the present position and future prospects of the potentialities of the study of trapped free radicals.

Broida, Herbert P. and Maurice Peyron, "Evaporation of Active Species Trapped in a Solid Condensed from 'Discharged' Nitrogen", J. Chem. Phys., 28, 725-726, (1958).

This investigation demonstrated that it was possible to transport, presumably atomic nitrogen, the active species from one surface through a 40-cm vacuum space to another surface. The experimental arrangement is shown in Figure 1 of the paper. The power source was a 2450-Mc/sec electrodeless discharge. The active species was collected on a Pyrex surface maintained at about $20^{o}K$ by liquid hydrogen.

It was observed that when both liquid hydrogen and liquid helium were present, all the products appeared to collect on the first surface. The second Pyrex surface was maintained near $1.2^{o}K$ by liquid helium. The solid on the first surface was removed by evaporation by removing the liquid hydrogen. If the evaporation from the first surface occurred within a few seconds after the deposition, the green emission from the second surface occurred. If the evaporation took place several minutes after the initial deposition, the solid deposited on the second cold surface gave only a very faint blue emission. This later phenomenon was taken

to indicate that another active species may have been transported from the first surface.

Carleton, N.P. and T.R. Lawrence, "Absolute Cross Sections for Excitation of Nitrogen by Protons of a few Kev Energy", Phys. Rev., 109, 1159-1165, (1958).

One reason for the measurement of cross sections for excitation by proton impact is the quantitative interpretation of auroral spectra. The authors state that at least part of the primary excitation of the aurora is due to fast protons entering the atmosphere from the outside. Therefore the mechanism of excitation of molecules of atmospheric gases by protons is of interest. The apparatus and method of measurement are fully described.

Cross sections for O, O first negative band of N_2^+ at λ 3912 A for the 2, 0 Meinel band of N_2^+ at λ 7850 A, and for a group of N I lines at about λ 8216 A were included in the measurements. The results are shown in many graphs included in the paper.

Dalgarno, A., "The Altitudes and Excitation Mechanisms of the Night Airglow", Ann. Geophys., 14, 241-252, (1958).

In this excellent review of excitation mechanisms of the night airglow Dalgarno adds for the sake of completeness a brief statement about identification of the first negative system of N_2^+ and the λ 5199 A line of atomic nitrogen. Reference is made to the mechanism proposed by Bates [Ann. Geophys, 8, 194, (1952)] that the 5199 A radiation may occur at twilight by

the following recombination

$$N_2^+ + e^- \rightarrow N(^2D) + N'$$

The persistence into the night according to Garstang is due to the long radiative lifetime of $N(^2D)$, 27 hours.

Eriksson, Karl Borge S., "Revised Energy Levels for the Neutral Nitrogen Atom", Arkiv. Fysik, 13, 429-439, (1958).

The author used in this study a pulsed electrodeless discharge as a light source. The wavelengths were determined by means of large concave-grating spectrographs. 110 lines of atomic nitrogen were photographed in the infrared and 8 lines in the visible. 16 lines in the vacuum ultraviolet between 1745 and 1134 A were obtained. The new terms 3d ^{4}p, 3p' ^{2}F, 5p ^{2}D, 3s'' ^{2}S, and 3d' ^{2}G were established. Extensive tables (Tables 1, 2, 3, 4, 5, and 6) give the measured and quoted wavelength, the observed and calculated wave-number, and the combination of these lines. Excellent plates of spectrograms obtained with a 21-foot wood-grating in a stigmatic mounting and in electrodeless discharge with a 21-foot Rowland grating are included in the paper. The light source, spectrograph, and interpretation of energy levels are discussed. A list of 24 literature references is included.

Foner, S.N., C.K. Jen, E.L. Cochran, and V.A. Bowers, "Electron Spin Resonance of Nitrogen Atoms Trapped at Liquid Helium Temperature", J. Chem. Phys., 28, 351-352, (1958).

The electron spin resonance spectrum of nitrogen atoms trapped in a molecular nitrogen matrix at liquid helium temperature was studied. Other solid matrices used in this investigation were hydrogen and methane. The electronic g-factor remained essentially constant for H_2 and CH_4 and was slightly lower than the g_J value reported for the free nitrogen atom. The authors conclude on the basis of their results that the departure of the hyperfine coupling constant for the trapped nitrogen atom from that of a free atom is very largely attributable to the influence of the matrix field.

Fontana, B.J., "Thermometric Study of the Frozen Products From the Nitrogen Microwave Discharge", J. Applied Phys., 29, 1668-1673, (1958).

The author states that there is adequate proof that nitrogen atoms are stabilized in a solid matrix at sufficiently low temperatures. The present research was a thermometric study of the phenomena accompanying the stabilization and the recombination of free nitrogen atoms in a solid nitrogen matrix at the temperature of liquid helium.

Particular attention is called to the fact that initiation of energy release in the deposited solid states starts at about $9^{\circ}K$, which is well below the apparent maximum temperature of about $20^{\circ}K$ during deposition. Another observation on heat evolution and light emission revealed that free nitrogen atoms persist in the solid phase up to about $36^{\circ}K$. This maximum temperature at which any visible glow was observed coincides with a thermal transition temperature in solid molecular nitrogen. It is suggested that the rearrangement of the crystal structure could completely

end the stabilizing effect of the solid matrix.

Harteck, P. and S. Dondes, "Formation of Nitrous Oxide from Nitrogen Atoms", J. Chem. Phys., 29, 234-235, (1958).

The purpose of the present paper is a reply to a remark made in a paper by Kistiakowsky and Volpi [J. Chem. Phys., 27, 1141, (1957)] implying that Harteck and Dondes [J. Chem. Phys., 24, 619, (1956)] had not considered the formation of nitrous oxide when free atoms are present.

Harteck and Dondes restate their conclusion that one of the major points in understanding the kinetics of the oxygen-nitrogen system are reactions (a), (b), and (c) in Table I which follows:

		$2\ NO$	(a) $k_1 = -13.3 \pm 0.5/cm^3$
$N + NO_2$	$\rightarrow$	$N_2O + O$	(b) $k_2 = -13.5 \pm 0.5/cm^3$
		$N_2 + 2\ O$	(c) $k_3 = -13.7 \pm 0.5/cm^3$
$2\ NO + O_2$	$\rightarrow$	$2\ NO_2$	(d) $k_4 = 37/cm^6$
$N + NO$	$\rightarrow$	$N_2 + O$	(e) $k_5 = -12.5/cm^3$
$O + NO_2$	$\rightarrow$	$NO + O_2$	(f) $k_6 = -12/cm^3$
$NO_2 + O$	$\rightarrow$	$NO^* + O_2$	(g)
			(k in $\log_{10}$ values)
$NO^* + NO_2$	$\rightarrow$	$N_2O + O_2$	(h)

Harteck and Dondes state that they disagree with Kistiakowsky and Volpi only in equations (g) and (h) which are ruled out as a possible mechanism for the production of nitrous oxide either

in the atmosphere or upon irradiating an oxygen-nitrogen mixture. The authors give the following references to their previous papers on the study of nitrogen atoms reacting with oxygen and the oxides of nitrogen.

(a) J. Chem. Phys., 22, 953, (1954).

(b) Phys. Rev., 95, 320, (1954).

(c) Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Vol. 14, p. 176, Geneva, (1955); United Nations, New York, (1956).

(d) Nucleonics, 14, 3, 66, (1956).

(e) J. Chem. Phys., 24, 619, (1956).

(f) J. Chem. Phys., 27, 546, (1957).

Harteck, Paul, Robert R. Reeves, and Gene Mannella, "Rate of Recombination of Nitrogen Atoms", J. Chem. Phys., 29, 608-610, (1958).

This is a report of experiments in which the rate of recombination of nitrogen atoms by a three-body collision process was determined.

$$N + N + M \xrightarrow{k} N_2 + M$$

The third body was nitrogen or argon and the rate was found to be same for both gases. The rate coefficient k was calculated to be

$$k = 1.72\ (\pm 0.17) \times 10^{-32}\ cm^6/molecules^2\ sec.$$

Reference is made to Mitra's [Phys. Rev., 90, 516-521, (1953)] later theory that active nitrogen is a mixture of nitrogen atoms in the ground state ^4S and the metastable states ^2D and ^2P produced by dissociative recombination of N_2^+ ions with electrons

which are always present in a strong electric discharge in nitrogen. The work of Kistiakowsky and Volpi is also cited in which they indicated the possibility of titrating nitrogen atoms with nitric oxide.

The atom concentration was determined in the present paper by the titration method. The reaction

$$N + NO \rightarrow N_2 + O$$

was found to be essentially instantaneous. The relative light intensities were measured from a photomultiplier. The experimental details are fully described as well as the color changes in the gas stream. When the nitrogen atoms were consumed the oxygen atoms reacted according to the following reaction

$$NO + O \rightarrow NO_2 + h\nu \quad \text{(continuum)}$$

yielding a whitish afterglow. A discussion is included to account for the results. The authors state that according to Gaydon and other investigators the most plausible explanation for the nitrogen afterglow begins with the three-body reaction

$$N(^4S) + N(^4S) + M \rightarrow N_2(^5\Sigma_g^+) + M$$

Herron, John T., J. L. Franklin, Paul Bradt, and Vernon H. Dibeler, "Kinetics of Nitrogen Atom Recombination", J. Chem. Phys., 29, 230-231, (1958).

Reference is made to the paper of Berkowitz, Chupka, and Kistiakowsky [J. Chem. Phys., 25, 457, (1956)] who determined that the nitrogen afterglow intensity was related to the disappearance of nitrogen atoms by a three-body process having a rate constant

of $7 \times 10^{14} (\times 10^{+2})$ cc^2 $mole^{-2}$ sec^{-1} (or 2×10^{-33} cc^{-2} $molecule^{-2}$ sec^{-1}). In the present paper the investigators have measured the rate of recombination by observing the decay of the nitrogen atoms in a flow system. The method consisted in "titrating" the N atoms with excess NO_2 injected at various distances from the microwave discharge, the source of the N atoms. The pressure was from 1 to 10 mm Hg; above about 3 mm the reaction was essentially a homogeneous third-order

$$-\frac{d[N]}{dt} = k_1 [N]^2 [M]$$

where [N] and [M] are, respectively, the concentrations of nitrogen atoms and third-body. The rate constant k_1 for the homogeneous reaction was calculated to be 5.4×10^{15} cc^2 $mole^{-2}$ sec^{-1} at $297^\circ K$. The rate constant was independent of the temperature in the range $273^\circ K$ to $453^\circ K$. This independence of the rate constant with temperature disagrees with the experiment of Frost, Evans, and Winkler [J. Phys. Chem., 61, 320, (1957)] who found the rate constant to decrease approximately as $k \propto T^{-4}$ with increasing temperature. The authors of the present paper maintain that the reaction is independent of temperature because of their method of direct measurement.

Hertzberg, Martin, "Atomic Nitrogen Projection of Ion-Atom Interchange Reactions in the Upper Atmosphere", J. Geophys. Res., 63, 856-859, (1958).

The significance of the ion-atom interchanges represented by the general reaction

$$X^{+} + YZ = XY' + Z$$

in F-layer recombination was first described by Bates [Proc. Phys. Soc. (London), A68, 344, (1955)]. Reference is also made to Potter's observation [J. Chem. Phys., 23, 2462, (1955)] that mass 30 occurred in a spectrum of air. Since the appearance potential of atomic oxygen ion was approximately that of atomic oxygen, the reaction

$$O^{+} + N_2 = NO^{+} + N, \quad \Delta E = 1.1 \text{ ev}$$

was assumed to explain the presence of mass 30.

The following exothermic reactions between the neutral species O, N, N_2, O_2, NO and the ions O^{+}, O_2^{+}, NO^{+} are considered.

$$O^{+} + N_2 = NO^{+} + N \qquad \Delta E = 1.1 \text{ ev} \qquad \text{(a)}$$

$$O^{+} + O_2 = O_2^{+} + O \qquad \Delta E = 1.4 \qquad \text{(b)}$$

$$O_2^{+} + N = NO + O^{+} \qquad \Delta E = 0.0 \qquad \text{(c)}$$

$$O_2^{+} + N = NO^{+} + O \qquad \Delta E = 4.3 \qquad \text{(d)}$$

$$O_2^{+} + N_2 = NO^{+} + NO \qquad \Delta E = 1.2 \qquad \text{(e)}$$

Assuming night-time equilibrium for the O^{+} ion concentration, the following equation is obtained

$$\frac{d(O^{+})}{dT} = O = -k_I(O^{+})(N_2^{+}) - k_{II}(O^{+})(O_2) + k_{III}(O_2^{+})(N)$$

From this expression the ratio of atomic to molecular oxygen ions is obtained

$$\frac{(O^{+})}{(O_2^{+})} = \frac{k_{III}(N)}{k_{II}(O) + k_I(N_2)} \qquad \text{(f)}$$

with the assumption that

$$k_I \sim k_{II} \sim k_{III}$$

The conclusion may be drawn that in the absence of ionizing mechanisms the ratio (O^+) / (O_2^+) should be small at all altitudes where N_2 and/or O_2 are major constituents unless a reasonable fraction of the N_2 is dissociated.

In Figure 1 in the paper curve A shows the relative concentrations of (O^+) / (O_2^+) obtained during a night-time rocket flight at Fort Churchill by Johnson and co-workers at NRL [J. Geophys. Res., 63, 443, (1958)]. Curve B was computed by the use of (f) from the data of Miller [J. Geophys. Res., 62, 351, (1957)], while curve C is computed by assuming that the ratio (N) / (N_2) is 10 times greater than the value given in the data by Miller.

The author states that the results interpreted in this manner indicate a larger concentration of atomic nitrogen than was heretofore considered to exist at these altitudes.

The following processes are considered

$$O^+ + N_2 = NO^+ + N \qquad \text{(a)}$$

$$N_2^+ + e^- = N' + N'' \qquad \text{(g)}$$

It is concluded that since the rocket results indicate a value for (O^+) / N_2^+ greater than 10, the rate of atomic nitrogen production from process (a) is of the order of a thousand times more rapid than the rate of production by process (g). The importance of process (a) is thus emphasized.

Istomin, V.G., "Investigation of the Ion Composition of the Earth's Atmosphere with Rockets and Satellites", National Academy of Sciences, (1958).

This paper was presented at the Rocket and Satellite Symposium during the Fifth Reunion of the Comite Special Annee Geophysique Internationale held in Moscow, 30 July to 9 August 1958. The investigation of the ion composition of the atmosphere was accomplished by means of a 7-5 stage radio-frequency mass spectrometer of the Bennett type. The launching was made after sunset on 9 September 1957.

The results revealed the presence of positive ions of atomic oxygen mass 16 and mass 30 (presumably NO^+) at altitudes from 105 to 190 km. The mass number 30 predominated from 105 to 206 km. Graph 1 in the paper clearly shows a maximum at 143 km formed by ions of mass 30.

The results of radio-frequency mass-spectrometers installed in Sputnik III from preliminary results of data showed that the predominating component is ions of atomic oxygen (mass 16) at altitudes of 250 to 950 km. Ions with a mass number of 14 of atomic nitrogen N^+ formed the second component of the ionosphere. The peak intensity of the ion current of mass 14 was found to be from 3 to 10 percent of the peak of ion current of mass 16 with a trend of increase with increasing altitude as given in the following table:

Height Km	230	250	255	285	385	460	650	705	820
iN^+ / iO^+	0.037	0.03	0.035	0.045	0.06	0.06	0.07	0.07	0.06

In addition to the mass peaks of ions O^+ and N^+, there were mass peaks which could be attributed to H_2O^+ (mass 18) and NO^+ (mass 30).

Jackson, Julius L., "Stabilized Free Radicals", J. Washington Acad. Sci., 48, 181-185, (1958).

The author in the present paper gives a brief summary of methods for producing and stabilizing free radicals. The techniques for detection and estimation of percentages of radicals of species trapped are also discussed. One method for producing free radicals involves providing energy great enough to break chemical bonds in the gas while the gas is enroute to a cold condensing surface. The energy may be supplied by microwave discharge, photolysis, and heat.

Absorption and emission spectra in all frequency ranges may be employed to identify the species present. Calorimetric experiments are performed to measure the amount of chemical energy stored in the free radical mixtures. Measurements of electric and magnetic susceptibilities are also used. A most important technique for detection involves that of electron spin resonance. The absorption of microwave energy by a sample is observed as a function of an externally applied magnetic field. By this method the detailed shape of the magnetic absorption spectrum identifies the radical that absorbs the radiation. Free radicals generally have unpaired electron spins, and as a result have large net magnetic moments.

Jennings, K.R. and J.W. Linnett, "Active Nitrogen", Quarterly Reviews, 12, 116-132, (1958).

This is an excellent and thorough review of active nitrogen beginning with the discovery in 1900 by Lewis that when nitrogen is subjected to an electrical discharge at low pressures a brilliant glow is emitted, and when the discharge is switched off a golden-yellow afterglow remains for several seconds. The review continues through the 1950's and includes the very recent work of Broida and co-workers on the study of active nitrogen at liquid helium temperatures. The following is an outline of the topics considered in this review.

1. Summary of early work.

   (a) production of active nitrogen, (b) kinetics of decay of the afterglow, (c) emission spectrum of the afterglow, (d) electrical properties of the afterglow, (e) excitation of spectra and chemical reactions, (f) energy measurements, and (g) other results.

2. Theories of Active Nitrogen.

   (a) the atomic theory, (b) Cario and Kaplan's theory, (c) Mitra's theory, (d) evidence against Mitra's theory, and (e) evidence against Cario and Kaplan's theory.

3. Evidence supporting the presence of ground-state atoms in the afterglow.

4. Recent work on the afterglow.

5. Explanation of the afterglow.

6. Active nitrogen at very low temperatures.

   (a) the α-lines, (b) the β-lines, (c) the A-bands, and (d) the Vegard-Kaplan bands.

7. Chemical Reactions of Active Nitrogen.

8. Conclusions.

(a) charged particles play no part in the production of the afterglow, (b) the only species present in active nitrogen in appreciable concentrations are atoms and molecules in the ground state, and (c) the predissociation theory succeeds in explanation of experimental observations and is able to account for the different band systems of the afterglow.

Johnson, C. Y., J. P. Heppner, J. C. Holmes, and E. B. Meadows, "Results Obtained with Rocket-Borne Ion Spectrometers", Ann. geophys., 14, 475-482, (1958).

During a night-time rocket flight a mass spectrometer which was carried to an altitude of 115 km recorded a positive peak for mass 28^+ (N_2). A day-time flight reaching an altitude of 113 km recorded only negative ion masses of 46^- (NO_2), 32^- (O_2), 22^- (?), and 16^- (O). During a flight to 251 km, along with other positive masses, those of 14^+ (N) and 28^+ (N_2) were recorded while the rocket was above 90 km.

Kaplan, Joseph and Charles A. Barth, "Chemical Aeronomy", Proc. Nat'l. Acad. Sci. U.S., 44, 105-112, (1958).

The authors state that the sun's radiation in the visible and infrared spectral regions is approximately that of a black body at 5800°K. In the spectral region from 1300 to 1750 A the solar continuum corresponds to a cooler black body and approximates a black body at 4500° K.

The following are reactions which involve atomic nitrogen in the upper atmosphere. Those accounting for the formation of nitric oxide (NO) are

$$N + O_2 \rightarrow NO + O \qquad (a)$$

$$N + O + M \rightarrow NO + M \qquad (b)$$

$$N + O_3 \rightarrow NO + O_2 \qquad (c)$$

The chemical reactions which remove nitric oxide and nitrogen dioxide from the upper atmosphere are (1) the photodissociation of nitric oxide by radiation less than λ 1900 A

$$NO + h\nu \rightarrow N + O \qquad (d)$$

and (2) the reactions of nitric oxide and nitrogen dioxide with atomic nitrogen.

$$NO + N \rightarrow N_2 + O \qquad (e)$$

$$NO_2 + N \rightarrow N_2 + O + O \qquad (f)$$

The above reactions indicate that reactions (a) and (e) govern the concentration of nitric oxide in the upper atmosphere. Reference is made to the rocket-seeding experiment by scientists at the Geophysics Research Directorate of the Air Force Cambridge Research Center who released ethylene into the upper atmosphere. The resulting luminescence indicated the presence of atomic nitrogen at the altitude of the emission.

Kaufman, Frederick, "Origin of Afterglow in Mixtures of Nitrogen and Oxygen", J. Chem. Phys., 28, 992, (1958).

In this letter to the editor Kaufman offers an explanation for why active nitrogen produces excited NO (β and γ systems) whose N is not that of the NO originally added past the discharge but

rather comes from the active nitrogen. This observation had been reported by Kaufman and Kelso [J. Chem. Phys., 27, 1209, (1957)] in a former communication to the editor of Journal of Chemical Physics.

Kaufman, Frederick and John R. Kelso, "Vibrationally Excited Ground-State Nitrogen in Active Nitrogen", J. Chem. Phys., 28, 510-511, (1958).

The authors remark that there is much evidence that ground-state N atoms, ^4S, are the principal species present in active nitrogen, and that they are responsible for the afterglow and its chemical reactivity. It is the purpose of this paper to present evidence for the presence of N_2* and to show how either $N(^4S)$ or N_2* can be preferentially destroyed; consequently their reactions may be examined separately.

A brief description is given of the instrumentation and method of experimentation. The reaction between N and NO is known to be very fast. An equivalent amount of NO was added upstream to extinguish the nitrogen afterglow and the blue NO glow, but not enough to produce the greenish-yellow air afterglow. Simultaneously N_2O was added downstream and the heat released was measured downstream. The heat was observed to be larger than in the absence of NO.

Two possibilities were suggested for an explanation: (a) N_2* is unaffected by NO; and (b) the reaction between N and NO gives rise to vibrationally excited nitrogen molecules. The authors concluded that the addition of NO removed ground-state nitrogen

atoms without destroying excited molecular nitrogen molecules, while the addition of N_2O removes excited molecular nitrogen molecules without affecting nitrogen atoms. The observations support the view of the existence of vibrationally excited nitrogen molecules in active nitrogen.

Kiess, N.H. and H.P. Broida, "Emission Spectra from Mixtures of Atomic Nitrogen and Organic Substances", 7th Symposium on Combustion, 28 August - 3 September 1958, held at London and Oxford, Butterworth's Scientific Publications, 207-214, (1958).

The purpose of this investigation was to study the effects of pressure and organic material on the electronic, vibrational, and rotational intensity distributions in the CN emission from "active" nitrogen flames. The relative intensity of the CH emission was also measured.

The experimental details are fully discussed. The nitrogen afterglow was obtained by means of an electrodeless discharge maintained by a 2450-megacycle magnetron power supply. A diagram of the discharge and atomic "flame" apparatus is shown in Figure 1 of the paper.

The results of the special intensities in various atomic nitrogen flames are summarized in Table 1. Several spectrograms are also included as well as spectral tracings obtained with a grating monochromator. A bibliography of seventeen references is given.

Kistiakowsky, G.B. and G.G. Volpi, "Reactions of Nitrogen Atoms.

II. H_2, CO, NH_3, NO, and NO_2", J. Chem. Phys., 28, 665-668, (1958).

In the second of this series of papers Kistiakowsky and Volpi have described their laboratory experimental details and the results of the reaction of atomic nitrogen with H_2, CO, and NH_3. In the first paper of the series it was found that the reactions of atomic nitrogen with NO and NO_2 were too fast for measurement.

The latter reactions were reexamined with a modified flow apparatus. The reactions of atomic nitrogen with NO and NO_2 were again found to be too fast for measurement. However making certain assumptions, the rate constant of the reaction

$$N + NO \rightarrow N_2 + O$$

was found to be larger than 5×10^{13} cc/mole sec. The same lower rate constant was deduced for NO_2, but the results were less certain.

Krasovskii, V.I., "Some Properties of the Solar Corpuscular Emission from the Spectra of Auroras", Astron. Zhur., 35, 222-226, (1958).

In this paper the author gives the characteristics of low-latitude auroras. Among other properties there is the appearance of the forbidden radiation λ 5200 A of atomic nitrogen. Reference is made to the ionized helium of solar corpuscular streams which causes some of the recharged neutral nitrogen emission.

Krassovsky, V.I., G.I. Galperin, A.V. Mironov, V.S. Prokudina,

N.N. Shefov, N.I. Fedorova, and B.A. Bagariazky, "Results from Studies of the Night Airglow and Aurorae in the U.S.S.R.", Ann. geophys., 14, 356-367, (1958).

This is a communication presented before the assembly of the International Union of Geodesy and Geophysics, held at Toronto, Canada, in September 1957. The authors reported that they had photographed several night sky spectras at Zvenigarod in which the N I line at 5200 is shown although there was no auroral or magnetic disturbance at the time. They also reported that spectrograms had been obtained which showed twilight flashes of the N_2^+ emission at about 3914 A.

Krassovsky, V.I., "The Nature of Emissions in the Upper Atmosphere", Ann. Geophys., 14, 395-413, (1958).

In this review of the nature of emissions in the upper atmosphere under the topic, Aurorae, the author refers specifically to atomic nitrogen. Table 3 in the paper contains some information on the ions of nitrogen atoms and molecules.

	N^+			N_2^+	
State	E	ΔE	State	E	ΔE
^3P	14.5	1.0	$^2\Sigma$	15.6	2.0
^1D	16.5	2.9	$^2\Pi$	16.7	3.1
^1S	18.6	5.0	$^2\Sigma$	18.7	5.2

E in ev's denotes the exciting energy of the state given in the table, while ΔE is the surplus energy compared with the ionization energy of a hydrogenation. Three features are given for the top

part of polar aurorae radiation.

(a) Relatively weak bands of neutral and ionized nitrogen molecules.

(b) Preponderance of the O I emission at 6300 A over the O I emission at 5577 A.

(c) The appearance of tne strongly forbidden N I radiation at 5200 A.

The following chain of elementary reactions is given to account for the main auroral features.

$$O^{+}(^{2}D) + N(^{4}S) \rightarrow N^{+}(^{3}p) + O(^{1}D) \quad (+\ 0.45\ ev)$$

$$O^{+}(^{2}p) + N(^{4}S) \rightarrow N^{+}(^{3}p) + O(^{1}S) \quad (-0.10\ ev)$$

$$O^{+}(^{2}D) + N(^{4}S) \rightarrow N(^{2}D) + O^{+}(^{4}S) \quad (-0.16\ ev)$$

$$N(^{2}D) = N(^{2}p) + h\nu \ (\lambda\ 10400\ A)$$

$$N(^{2}p) = N(^{4}S) + h\nu \ (\lambda\ 5200\ A)$$

Le Blanc, F., Y. Tanaka, and A. Jursa, "New Band Systems in the Afterglow of Nitrogen", J. Chem. Phys., 28, 979-981, (1958).

The lower state of the new bands was believed to be the $B\ ^{3}\Pi_{g}$ since this was in excellent agreement between observed and calculated ΔG values. A Deslandres table of the new system (cm^{-1}) is included, and three photographs of the new N_2 bands are shown in Figure 1. Three prominent heads, easily observable, were measured and analyzed. The results are given in Table 1, a Deslandres table. Some interesting features of the appearance of the bands are noted and pointed out.

Meadows, E. B. and J. W. Townsend, Jr., "Diffusive Separation

in the Winter Night Time Arctic Upper Atmosphere 112 to 150 Km", Ann. Geophys., 14, 80-93, (1958).

With regard to atomic nitrogen, the data obtained during this rocket flight on 20 November 1956 at Fort Churchill, Manitoba, Canada, showed no great change in the N/N_2 ratio as compared with that obtained by calibration. It was concluded that no information concerning the presence of atomic nitrogen in this altitude range had been obtained.

Nicolet, M., "High Atmosphere Densities", Science, 127, 1317-20, (1958).

When atomic nitrogen is produced in the thermosphere it reacts immediately, above 110 km, with molecular oxygen according to the process $N + N \rightarrow N_2 + O$, and disappears by the reaction $NO + N \rightarrow N_2 + O$. The life-time of a nitrogen atom is less than one day at altitudes below 200 km. Therefore there is insufficient dissociation of nitrogen, and any working model of the atmosphere can incorporate atomic nitrogen only as a minor constituent, while the concentration of nitric oxide is a definite fraction of the concentration of molecular oxygen in the whole atmosphere. On this basis the author concludes that the Rocket Panel model is not acceptable. A temperature of $2250^{\circ}K$ at 500 km leads to densities not less than 4×10^{-15} g/cm^3 at 500 km.

Saporoschenko, Mykala, "Ions in Nitrogen", "Phys. Rev., 111, 1550-1553, (1958).

The following ions N^+, N_2^+, N_3^+, and N_4^+ have been identified in nitrogen gas by means of a mass spectrometer. The ultimate

pressure in the system was 1.5×10^{-6} mm Hg prior to the introduction of the experimental gas. The ion source was operated in the pressure range from 10^{-3} to 0.6 mm Hg.

It was found that the onsets of ionization occur at 15.5 ± 0.2 ev for N_2^+, 15.8 ± 0.3 ev for N_4^+, 22.1 ± 0.5 ev for N_3^+, and 24.2 ± 0.4 ev for N^+.

From an analysis of the experimental measurement it was suggested that the N_4^+ may be formed as follows:

(a) $N_2^* + N_2 \rightarrow N_4^{+*}$ (vibrationally excited)

The appearance potential of 22.1 ev of N_3^+ suggested that the reaction may be

(b) $N_2^{+*} + N_2 \rightarrow N_3^+ + N$ where N_2^{+*} is an ion excited possibly to the negative band system of N_2^+ with origin at 1847 A or 6.7 ev above the ground state of N_2^+, or 22.276 ev above the ground state of N_2. It is also shown that in reaction (b) a nitrogen atom is released which constitutes a form of dissociation of N_2, thus accounting for the value of the dissociation energy of 7.38 ev found by some observers. The present analysis shows that atomic nitrogen is formed at 22.1 ev as a by-product of the N_3^+ formation and at 24.3 ev as a by-product of the N^+ formation. It is pointed out that the mode of formation of free atomic nitrogen probably depends on p, E/p, and available electron energies. The first reaction would give a value for $D(N_2) = 7.3$ ev, while the latter would lead to 9.76 ev for the value of $D(N_2)$

Thouvenin, J., "Dissociation et Ionisation de L'air par Une Onde de Choc", J. Phys. radium, 19, 639-648, (1958).

The temperature range was from 3500 to 11500°K and the density was from 4 to 12 times that of normal. Oxygen was observed to be completely dissociated by strong shock waves with velocities above 7000 m sec^{-1}, and the nitrogen by a rate of 50 percent higher. The concentration of free electrons was over 0.1 percent.

Watanabe, K. "The Ultraviolet Absorption Spectrum of Nitrogen", Advances in Geophysics, edited by H.E. Landsberg and J. Van Mieghem, Vol. 5, pp. 185-190, Academic Press Inc., New York, (1958).

The author states that the nitrogen absorption spectrum down to 800 A consists for the most part of sharp bands which demand high-resolution photometry. In the spectral region from 1000 to 1450 A, the absorption spectrum is comprised chiefly of the Lyman-Birge-Hopfield Bands. These correspond to the forbidden transition a $^1\Pi_g \leftarrow X\ ^1\Sigma_g^+$ and are very weak. Reference is made to the bands observed at λλ 1123.4, 1098.9, and 1075.6 A by Tanaka, who suggested that they are the first three bands of the transition $C\ ^3\Pi_u \leftarrow X\ ^1\Sigma_g^+$.

The author points out that the absorption cross-section, σ, values of nitrogen are of special interest to the study of the upper atmosphere in the Lyman-α and Lyman-β regions. Ditchburn, Bradley, Cannon, and Munday (1954) obtained a value of 6×10^{-23} cm^2 for σ for an upper limit at Lyman-α using an equivalent path length of 500 atoms-cm.

The spectral region λλ 800 to 1000 A which is extremely complicated is briefly discussed. Figure 14 in the paper shows

a semiquantitative absorption cross-section plot of N_2 in this region. Recent studies have failed to show a continuum in this spectral range.

The spectral region below 800 A is also briefly considered. Reference is made to the new Rydberg series converging to the a $^2\Pi$ state of N_2^+ at 16.94 ev above the ground state of N_2, as found by Worley (1953). The value of the absorption cross-section at the helium resonance line at λ 584 A as determined by Astoin and Granier (1957) is in good agreement with the values 1.8×10^{-17} cm^2 and 1.9×10^{-17} cm^2 measured by Clark (1952) and Marmo, respectively.

Wentink, Tunis, Jr., John O. Sullivan, and Kurt L. Wray, "Nitrogen Atomic Recombination at Room Temperature", J. Chem. Phys., 29, 231-232, (1958).

This is a report of the measurement of atomic recombination rates in pure N_2 at room temperature in a nonflow system. The experimental method used is fully described. A hot-wire signal was employed to measure the rate of disappearance of atoms into all possible molecular states.

The data was reduced in terms of the following:

$$\frac{d[N]}{dt} = -2K[N]^2[N_2] - K_w[N],$$

where K_w is a measure of the atom loss due to recombination at the wall; and

$$I = K_{ag}[N]^2[N_2]$$

where K_{ag} is the afterglow rate.

The authors report the following value for the rate constant,

$$2K = 1.2 \times 10^{16} \ cc^{2} \ mole^{-2} \ sec^{-1}$$

Zelikoff, Murray, Frederick F. Marmo, Jerome Pressman, Edward R. Manring, Leonard M. Aschenbrand, and Adolph S. Jursa,

"An Attempt to Measure Atomic Nitrogen by Rocket Release of Ethylene at 105 and 143 Km", J. Geophys. Research, 63, 31-37, (1958).

The authors describe an attempt to establish the presence of atomic nitrogen in the upper atmosphere by release of ethylene gas from an Aerobee rocket.

Nine pounds of ethylene were released at altitudes of 105 and 143 km. According to Versteeg and Winkler atomic nitrogen reacts with ethylene with the production of chemiluminescent CN bands. The intensity was crudely estimated through the use of Super-Schmidt meteor cameras with x-ray (blue sensitive) and Tri-X (red sensitive) film.

Table 1 in the paper gives the results of the photometric data. The authors conclude from their analysis of the data that the lower cloud at 105 km was produced by the reaction of atomic nitrogen with ethylene, and the upper cloud was caused by the reaction atomic oxygen with ethylene. The red color of the lower cloud at 105 km was postulated to be caused by the $N-C_2H_4$ reaction, while the $O-C_2H_4$ system should yield blue bands.

The authors concluded from their deductions that the upper cloud at 143 km was due to the reaction of atomic oxygen with the ethylene.

1959

Barth, Charles A., William J. Schade, and Joseph Kaplan, "Blue Nitric Oxide Afterglow", J. Chem. Phys., 30, 347-348, (1959).

The authors state that the blue nitric oxide afterglow and the orange nitrogen afterglow have some common characteristics. The upper limit of the energy of the afterglow emission is equal to the energy of recombination. According to present theory the spectrum produced by the afterglow has its origin in fully permitted transitions from excited states that cannot be formed directly by ground-state atoms. The production of ground-state atoms from an excited nitrogen molecule is an intermediate reaction followed by an inverse predissociation during a three-body collision.

The authors state that the purpose of the present paper was to report that an intensity shift occurs in the spectrum of the blue nitric oxide afterglow from the addition of a rare gas to the mixture. The present note suggests that the excitation mechanism of active nitrogen may occur in other reactions which involve the recombination of atoms.

Bates, D.R., "Discussion of Paper by F.D. Stacey, The Possible Occurrence of Negative Nitrogen Ions in the Atmosphere", J. Geophys. Research, 64, 2469, (1959).

In the paper by Stacey (1959) it was suggested that molecular nitrogen has an unstable negative ion which may be formed and destroyed by the radiationless process

$$N_2 + e^- \rightleftarrows N_2^-$$

Also, as a result, the disappearance of electrons at low gas densities (corresponding to the F_2 layer) follows an attachment law. Consequently the ion recombination process.

$$N_2^+ + N_2^- \rightarrow 2\, N_2$$

causes the effective recombination to be strongly pressure-dependent.

In the present note Bates points out that the supposed negative ions are far too rare to have these pressure effects. If the free electrons have a Maxwellian distribution at temperature T, then

$$n(N_2^-)\ /n(e^-) = \mu \quad n(N_2)$$

with $\mu = \dfrac{\omega_1}{2\omega_o} \left\{ \dfrac{h_2}{2\pi\ k\ mT} \right\}^{3/2} \quad \exp\ (\ -\epsilon/kT)$

in which n denotes the number densities, ω_1 is its excess energy with respect to the neutral molecule, k is Boltzmann's constant, and m is the mass of the electron. Taking the statistical weight factor ω_1/ω_o to be unity and ϵ to be zero, the above equation yields

$$\mu = 4 \times 10^{-16}/T^{3/2}\ \text{cm}^2$$

It is concluded that the negative ion to electron ratio is so minute that the possible formation of N_2^- may be completely neglected both in the ionosphere and in the laboratory work on recombination mechanisms.

Bates, D. R., "Some Problems Concerning the Terrestrial Atmosphere Above About the 100 km Level", Proc. Roy. Soc., A253, 451-462, (1959).

This paper is a survey of the general structure of the thermosphere with particular emphasis on the composition and temperature. It is part of a discussion on space research held 12 and 13 November 1958. Consideration is given to the significance of recent rocket and satellite studies. It is stated that hydrogen is very rare at the base of the exosphere unless hydrogen atoms are being captured very rapidly from interplanetary space. The following topics are discussed.

1. Composition
   A. Diffusive separation
   B. Photochemical action
2. Temperature
3. Thermal economy
   A. Loss
   B. Gain
      (1) Ultraviolet radiation
      (2) Corpuscular radiation
      (3) Solar corona

Appendix

An analytic model thermosphere at 120 km with the following composition is given, based on rocket data and other studies:

$n(O)$ 120 km $= 1.80 \times 10^{11}$ cm^{-3}

$n(O_2)$ 120 km $= 3.95 \times 10^{10}$ cm^{-3}

$n(N_2)$ 120 km $= 2.40 \times 10^{11}$ cm^{-3}

T 120 km $= 380^{\circ}$ K

Reference is made to the discoveries of Townsend, Johnson, Holmes, and Meadows (1958) and to Istomin (1958) that NO^+ is the dominant species of ion in the lower part of the F layer. However it is emphasized

that this does not mean that nitric oxide is abundant. The ions in question are not formed by photoionization of their parent molecules but rather through the collision process

$$O + N_2 \rightarrow NO^+ + N$$

According to Nicolet (1958) atomic nitrogen and nitric oxide are considered only minor constituents since their relative concentrations are insufficient to affect the mean scale height appreciably. Table 1 in the paper gives a tabulation of the number densities of atomic oxygen, molecular oxygen, and molecular nitrogen from 120 to 800 km. The temperature is shown to be isothermal from 250 to 800 km with a value of 1050° K.

Beale, G.E., Jr. and H.P. Broida, "Spectral Study of a Visible, Short-Duration Afterglow in Nitrogen", J. Chem. Phys., 31, 1030-1034, (1959).

In the present paper the authors have reported that an afterglow was found to occur 5 milliseconds after the discharge which differed from the usual Lewis-Rayleigh afterglow. The pink-colored glow persisted for about 2 milliseconds and was both preceded and followed by the usual yellow glow of active nitrogen.

It was observed that in the visible and near ultraviolet, the short-duration afterglow was characterized by strong emission of N_2 ($B\ ^2\Sigma_u^+ - X\ ^2\Sigma_g^+$) and N_2 first positive ($B\ ^3\Pi_g - A\ ^3\Sigma_u^+$) bands and weak emission of N_2 second positive ($C\ ^3\Pi_u - B\ ^3\Pi_g$) bands.

The degree of purity of the nitrogen was found to be very

important. The pink glow was not obtained by using ordinary nitrogen from commercially supplied cylinders or by the addition of 0.1 per cent of oxygen to purified nitrogen. The pink glow was not affected by strong magnetic fields.

The authors concluded that the excitation of emission in the pink region could not be accounted for on the basis of the known constituents of active nitrogen. The presence of highly energetic species other than nitrogen atoms after the discharge was indicated. It was postulated that metastable $^1\Pi$ states of molecular nitrogen are the best possible source of the short-lived active species responsible for this phenomenon.

Boyd, R. L. F., "Space Research", Nature, (London), 183, 361-364, (1959).

In this survey paper reference is made to the presence of atomic oxygen and atomic nitrogen in the upper atmosphere. The author states that above 100 km oxygen is largely dissociated, and at an altitude of 300 km atomic oxygen is probably ten times as abundant as atomic nitrogen. Below 300 km nitrogen is largely molecular due to the following rapid recombination reactions of atomic nitrogen.

$$N + O_2 \rightarrow NO + O$$

$$N + NO \rightarrow N_2 + O$$

According to Boyd the ionic composition up to 200 km is chiefly NO^+ probably formed by

$$O^+ + N_2 \rightarrow NO^+ + N$$

This paper was presented before a discussion on space research, held

12-13 November 1958 and arranged by the Royal Society.

Broida, Herbert P. and John R. Pellam, "Formation and Stabilization of Atoms and Free Radicals", U.S. Patent #2,892,766, June 30, 1959.

This U.S. Patent describes the preparation of atoms and free radicals in the solid state. Nitrogen gas at a pressure of 0.1 to 10 mm Hg is exposed to an electrodeless discharge excited by a microwave voltage (2450 Mc/sec). The atoms and radicals produced are condensed in a trap which is maintained at a temperature of 4.2°K by a liquid helium bath. The nitrogen gas yields a deposit on the walls of the trap and emits a strong green glow with occasional flashes of blue. The glow disappears suddenly between 4.2 and 77°K. When analyzed spectroscopically it was found to be identical with the glow produced by bombarding solid nitrogen with electrons. The deposit therefore consists of nitrogen atoms. The patent also covers other gases: oxygen, hydrogen, water vapor, and mixtures of nitrogen, oxygen, and hydrogen all of which give solids which are atoms or free radicals or a mixture of these with their molecules.

Camm, John C. and James C. Keck, "Experimental Studies of Shock Waves in Nitrogen", Research Report 67, Avco Everett Research Laboratory, Massachusetts, June 1959.

This research was supported jointly by Air Force Ballistic Missile Division, Air Research and Development Command, United States Air Force, and Army Rocket and Guided Missile Agency,

Army Ordnance Missile Command, United States Army.

The radiative relaxation behind shock waves in pure nitrogen was studied to determine rate constants for recombination of nitrogen atoms. The radiation was measured as a function of wavelength for conditions corresponding to $T = 6600^{o}K$ with $\rho = 0.018\rho_{o}$ and $T = 6300^{o}K$ with $\rho = 0.12\rho_{o}$.

The most prominent radiation in the wavelength interval studied was found to be associated with the $N_2^+(1-)$ and $N_2(1+)$ bands. For a mean value of $T = 6400^{o}K$, the recombination rate constant for nitrogen atoms is $<0.3 \times 10^{-32}$ cm^6 sec^{-1} when N_2 is the catalyst, and 2.4×10^{-32} cm^6 sec^{-1} when atomic nitrogen is the catalyst.

Carroll, P.K. and H.E. Rubalcava, "Near Infrared System of Nitrogen", Nature, 184, 119-120, (1959).

Reference is made to the discovery of a new triplet transition in the near infrared by Carroll and Sayers [Proc. Phys. Soc., A66, 1138, (1953)]. The four strongest heads of the new band appeared at λλ8265.5, 8283.8, 8293.3, and 8310.6 A. Bands of nitrogen in the infrared have also been reported by Kistiakowsky and Warneck [J. Chem. Phys., 27, 1417, (1957)] and by LeBlanc, Tanaka, and Jursa [J. Chem. Phys., 28, 979, (1959)]. The latter workers studied the emission from afterglows in argon-nitrogen mixtures at low temperatures.

The new system discussed in the present paper is considered to be of both theoretical and astrophysical interest since the 8265.5 A band has recently been investigated. The authors photographed it

in the second of the 21-foot grating in the Physics Department of University College, Dublin. A rotational analysis was made and is reported briefly in the present paper.

Dressler, K. "Absorption Spectrum of Vibrationally Excited N_2 in Active Nitrogen", J. Chem. Phys., 30, 1621-1622, (1959).

The research reported in the present paper is part of the research carried out under the National Bureau of Standards Free Radicals Research Program supported by the Office of Ordnance Research. Reference is made to the investigations of Kaufman and Kelso [J. Chem. Phys., 28, 510, (1958)] who reported that there was strong evidence for the presence of active nitrogen in appreciable quantities in molecular nitrogen in the first vibrationally excited state.

The author states that this interpretation is correct and that vibrationally excited ground-state nitrogen was positively identified in active nitrogen. The identification was accomplished by means of its vacuum ultraviolet absorption spectrum. The experimental apparatus, method of procedure, and conditions are fully described. The absorption lines of atomic nitrogen λλ1200.71, 1200.22, 1199.55, 1134.98, 1134.42, and 1134.17 A are reported to appear with great intensity on the spectrograms.

Dufay, Maurice, "Presence of the Forbidden ^4S - ^2D Line of the Nitrogen Atom in the Spectrum of the Night Sky", Compt. rend., 248, 2505-2507, (1959).

In the present paper the author reports that the $^4S \rightarrow {}^2D$ (5199 A) line of the neutral nitrogen atom was observed regularly in night sky spectra during 1958-1959. The 5199 A line of N I is partially superimposed on the 9 - 2 and 6 - 0 bands of OH. The intensity of the line appeared to be related to the geomagnetic planetary index and increased at the same time as that of the 6300-6363 lines of O I.

Dufay, Maurice, "Etude photelectrique du Spectre du Ciel Nocturne dans le Proche Infra-rouge", Ann. geophys., 15, 134-152, (1959).

This is a report of a study of the spectra of the night sky and the aurora in the near infrared. A scanning spectrometer equipped with a rotating grating and a Lallemand photmultiplier (refrigerated Cs-O-Ag photocathode) was used. The sensitivity of the instrument was such that recordings of the 0.7 - 1.1 μ region with a spectral slit of 15 A and a scanning period of 45 minutes could be obtained.

Among other emissions of several low latitude auroras, the atomic line of N I was studied. The forbidden transition $^2D \rightarrow {}^2P$ of N I (10,400 A) was observed to have a relatively great intensity. Table V in the paper lists the identifications. A bibliography of 30 references is included in the paper.

Duff, Russell E. and Norman Davidson, "Calculcation of Reaction Profiles Behind Steady State Shock Waves. II. The Dissociation of Air", J. Chem. Phys., 31, 1018-1027, (1959).

The authors have used a numerical integration procedure to investigate the reaction profile behind strong shock waves in air. The dissociation reactions for O_2, N_2, and NO are discussed along with the "shuffle" reactions

$$N + O_2 \rightleftarrows NO + O \text{ and } O + N_2 \rightleftarrows NO + N$$

The following five reactions were considered for most of the work.

$$O_2 + M \underset{k_1r}{\overset{k_1f}{\rightleftarrows}} O + O + M \qquad (a)$$

$$N_2 + M \underset{k_2r}{\overset{k_2f}{\rightleftarrows}} N + N + M \qquad (b)$$

$$NO + M \underset{k_3r}{\overset{k_3f}{\rightleftarrows}} N + O + M \qquad (c)$$

$$O + N_2 \underset{k_4r}{\overset{k_4f}{\rightleftarrows}} NO + N \qquad (d)$$

$$N + O_2 \underset{k_5r}{\overset{k_5f}{\rightleftarrows}} NO + O \qquad (e)$$

The recombination rate constants for the dissociation reactions (a), (b), and (c) were assumed to be 3×10^{14}, 3×10^{14}, and 6×10^{14} $(\text{moles cm}^{-3})^{-2}\ \text{sec}^{-1}$ respectively. The rate constants for the last two reactions $k_4f = 5 \times 10^{13} \exp(-75,500/RT)$ $(\text{moles cm}^{-3})^{-1}\ \text{sec}^{-1}$ and $k_5f = 1 \times 10^{11}\ T^{1/2} \exp(-6200/RT)$ $(\text{moles cm}^{-3})^{-1}\ \text{sec}^{-1}$ are those determined by Glick, Klein, and Squire [J. Chem. Phys., 27, 850, (1957)] and Kistiakowsky and Volpi [J. Chem. Phys., 27, 1141, (1957)] respectively.

The authors conclude that the reaction

$$N_2 + M \rightarrow N + N + M$$

makes only a very small contribution to the total N atom concentration.

Faire, A.C. and K.S.W. Champion, "Measurements of Dissociative Recombination in Nitrogen at Low Pressure", Phys. Rev., 113, 1-6, (1959).

The authors have extended their measurements [J. Applied Phys., 29, 928, (1958)] of the recombination coefficient of nitrogen ions to lower nitrogen pressures by using an inert gas to reduce diffusion losses. In addition to being basic microwave techniques, a monochromator and photomultiplier were employed to study the spectra emitted.

The topics considered in the present paper are (a) experimental procedure, (b) results for nitrogen only, (c) results for nitrogen and helium, (d) afterglow processes in nitrogen-helium mixtures, (e) analysis of afterglow data, and (f) higher diffusion modes.

The average values of the recombination and diffusion coefficients which the authors report from their experiments are, respectively, $\alpha = (4.0 \pm 0.3) \times 10^{-7}$ cm^3 sec^{-1} and $D_a p = 220 \pm 30$ cm^2 sec^{-1} mm Hg with an electron temperature of about 400°K. For pressures below 4 mm Hg the authors found that the value of α was independent of pressure. Acknowledgment is made to Miss Anna D. Gray for laboratory and computational assistance.

Fogel', Ya. M., V.F. Kozlov, and A.A. Kalmykov, (Translated

by H. Lashinisky), "On the Existence of the Negative Nitrogen Ion", Soviet Phys., (JETP), 36, (9), No. 5, 963-964, (1959).

The authors have considered the question of how the atoms in the periodic chart form stable negative ions. Experimental data seem to have established the following rule: atoms with unfilled electron shells form stable negative ions, while atoms with filled shells do not form negative ions. Only one exception to this rule has been observed at the present time, the nitrogen atom, which has a $2p^3$ configuration in its outer electron shell. Reference is made to the work of V.M. Dukel'shii and E. Ya. Zandberg [Doklady Akad. Nauk, SSSR, 86, 263, (1952)], O Tuxen [Z. Physik, 103, 463, (1936)], and L.M. Brandscomb and S.J. Smith [J. Chem. Phys., 25, 598, (1956)] who showed that N^- ions are not produced in a gaseous discharge in nitrogen. The authors state that the absence of N^- ions in the plasma of a gaseous discharge is not proof of the nonexistence of this ion; because of the low electron affinity of the nitrogen atom the density of negative nitrogen atoms in a plasma may be very small.

In the present investigation the authors have attempted to observe N^- ions resulting from the $N^+ \rightarrow N^-$ process in the passage of a beam of N^+ ions through matter. The search for N^- ions was made by employing a double mass spectrometer which had previously described [J. Exptl. Theoret. Phys. (U.S.S.R.), 29, 209, (1955); Soviet Phys., JEPT, 2, 252, (1956)]. A high-frequency ion source was used for obtaining N^+ ions. The beam of N^+ ions, with an energy of 34 kev, was analyzed by a magnetic mass monochromator and directed into the collision chamber which was filled with krypton.

The resolving power of the mass monochromator was sufficient for complete separation of the line at mass 14 from the nearby lines at 13 and 15. The beam which passed through the collision chamber was analyzed by means of a magnetic analyzer. The negative ion current was measured with a vacuum-tube voltmeter (sensitivity 10^{-14} amp/div). The first experiments, at a current of about 10^{-7} amp, indicated that the beam contained a small amount of negative ions of mass 14. The number of negative ions increased with increasing pressure of the krypton in the collision chamber.

The mass-spectrometer method was employed to measure the effective cross section for the $N^+ \rightarrow N^-$ process, which was estimated to be 1.1×10^{-22} cm^2. This extremely small cross-section value indicates that the binding energy of the excess electron in the N^- ion must be very small. This is in agreement with the estimates of Bates [Proc. Roy. Irish Acad., 51, 151, 1947)] by the study of negative ions by extrapolation through isoelectronic series.

The authors also made an attempt to observe negative molecular nitrogen ions. The $N_2^+ \rightarrow N_2^-$ process in krypton was used. It is reported that no N_2^- ions were observed and that the cross section for the $N_2^+ \rightarrow N_2^-$ process is smaller than 1.5×10^{-22} cm^2.

Fontana, B.J., "Magnetic Study of the Frozen Products From The Nitrogen Microwave Discharge", J. Chem. Phys., 31, 148-153, (1959).

The research work reported in this paper is a study of magnetic

susceptibility measurements made during the condensation of a mixture of atomic and molecular nitrogen produced in a microwave discharge. The magnetic effect was measured by an a. c. mutual inductance method.

It was estimated that not more than 0.01 to 0.04 mole percent free nitrogen atoms persisted in the solid phase. When more than one or two percent nitrogen atoms condense from the gas phase, essentially instantaneous recombination occurred. When a mixture of 0.5 percent or less of nitrogen atoms was condensed, from 0.2 to 0.5 mole percent free atoms could be stabilized for short periods of time, five minutes being the longest. The method of determining the concentration of N atoms is described.

Hammerling, P., J.D. Teare, and B. Kivel, "Theory of Radiation from Luminous Shock Waves in Nitrogen", Phys. Fluids, 2, 422-426, (1959).

In this paper the physical properties behind a normal shock wave in nitrogen are calculated as a function of time. These include the variation of temperature, composition, ionization, and the intensity of radiation from the N_2 first negative band system. The calculation incorporates a rate equation for the dissociation of N_2

$$N_2 + M \rightleftarrows 2N + M$$

subject to the constraint of the conservation equations. The authors state that the nitrogen dissociation rate is no known from experiments. Its recombination rate which was scaled according to a theory of Keck [J. Chem. Phys., 29, 410, (1958)] is listed as follows.

Reaction: $N + N + M \rightarrow N_2 + M$

When 3rd body (M) is N, the recombination rate is

$$k_{R,a} = 2.2 \times 10^{-27} T^{-1.5} \text{ cm}^6 \text{ sec}^{-1}$$

and when 3rd body (M) is N_2, the recombination rate is

$$k_{R,m} = 4.4 \times 10^{-28} T^{-1.5} \text{ cm}^6 \text{ sec}^{-1}.$$

The equations governing the chemistry are

$$\left(\frac{\delta[N_2]}{\delta t}\right)_\rho = -k_D [M] [N_2] + k_R [M] [N]^2 \qquad \text{(a)}$$

and

$$\frac{d \epsilon_v}{dt} = \frac{(\epsilon_v)eq - \epsilon_v}{\tau_v} \qquad \text{(b)}$$

where ϵ_v = the vibrational energy per molecule at time t, $(\epsilon_v)_{eq}$ = local equilibrium value, and τ_v = the vibrational relaxation time.

Harrison, A. W. and A. Vallance Jones, "Observations on Meinel N_2^+ Bands Near 1.5μ in the Auroral Spectrum", J. Atmos. Terrest. Phys., 13, 291-294, (1959).

This is a report of observations of the 0, 1 and 1, 2 Meinel bands of N_2^+ in the auroral spectrum at 1.46 and 1.53 μ. The results are listed in Table 1 in which the band, wavelength, and the calculated and observed brightness are recorded. The results suggest that the band originating in the v' = 1 vibrational level is abnormally strong as compared with the band originating from the vibrational level v' = O. The following reaction is given for this enhancement.

$$O + (^2D) + N_2 (X\ ^1\Sigma_g) \rightarrow O\ (^3P) + N_2^+ (A\ ^2\Pi_u, v' = 1)$$

Harteck, P. and S. Dondes, "The Kinetic Radiation Equilibrium of Air", J. Phys. Chem., 63, 956-961, (1959).

In this report Harteck and Dondes have discussed their recent studies of the irradiation of nitrogen-oxygen mixtures in the steady state of formation and the decomposition of the constituents.

A complex series of reactions takes place when mixtures of nitrogen and oxygen are irradiated. Ionizing radiation forms ions and excites and dissociates the gases. Through ion recombination additional molecules will dissociate. The following table is a list of reactions most important to the nitrogen fixation process.

(G - value = number of molecules formed per 100 ev)

(1)	$N_2 \rightarrow 2N$	G-value 4-5
(2)	$O_2 \rightarrow 2O$	G-value 8
(3)	$N + O_2 = NO + O$	$k_3 = 10^{-16} \pm 0.02$
(4)	$NO_2 + O = NO + O_2$	$k_4 = 10^{-12}$
(5)	$2\ NO + O_2 = 2\ NO_2$	$k_4 = 10^{-37} \pm 0.2$
(6)	$2\ NO_2 \rightleftharpoons N_2O_4$	
(7) (a)	$NO_2 \rightarrow NO + O$	$G = 12$
(b)	$NO_2 \rightarrow N + O + O$	$G = 0.5$
(8) (a)	$N + NO_2 = 2\ NO$	$k_{8_a} = 5 \times 10^{-14} \pm 0.5$
(b)	$N + NO_2 = N_2O + O$	$k_{8_b} = 3.2 \times 10^{-14} \pm 0.5$
(c)	$N + NO_2 = N_2 + 2O$	$k_{8_c} = 2 \times 10^{-14} \pm 0.5$
(d)	$N_2O_4 + N \rightarrow NO_2 + 2\ NO$	

(9) $NO + N \rightarrow N_2 + O$ $\qquad k_9 = 10^{-12} \pm 0.5$

(10)(a) $N_2O \rightarrow N_2 + O$ $\qquad G = 9$

(b) $N_2O \rightarrow NO + N$ $\qquad G = 3$ $\qquad \Big\} = 12$

(11) $NO \rightarrow N + O$ $\qquad G = 3$

(12)(a) $NO^+ + e^- = N + O$

(b) $NO^+ + e^- = NO + h\nu$

(c) $NO + M^+ = NO^+ + M$

(13) $N_2^+ + O_2 = NO^+ + NO$ (no indication)

$N_2^+ + NO_2 = N_2O + NO$ (no indication)

The G-values for dissociation processes as well as the rate coefficients (K-values) at $300^{\circ}K$ for the reactions which result from the dissociation products are given. Most of these reactions are fully explained in the discussion portion of the paper.

Herron, John T. and Vernon H. Dibeler, "Studies of the Evaporation of Condensates Containing Nitrogen Atoms", J. Chem. Phys., 31, 1662-1665, (1959).

In this study the products of an electrodeless discharge in nitrogen or mixtures of nitrogen in neon or argon were condensed at $4.2^{\circ}K$. Except for a brief communication by Broida and Peyron [J. Chem. Phys., 28, 725, (1958)] describing a qualitative experiment there seems to be no experimental data as to the extent to which highly energetic atoms or radicals may be removed from a condensed phase. It is the purpose of the present paper to report the results of a study in which nitrogen and mixtures of nitrogen and rare

gases, after passage through an electric discharge and condensation on a liquid helium cooled surface were re-evaporated and analyzed by means of a mass spectrometer.

The experimental details are described in full. The nitrogen atom sensitivity was determined experimentally. The ion current due to N^+ from N atoms was measured using the same electron energy (18 ev) as employed in monitoring the warm-up experiments. The nitrogen atom concentration in the discharge was approximately 1% as determined by titration with nitric oxide. The sensitivity of nitrogen atoms was calculated as the ion current per unit nitrogen atom pressure. The lower detection limit of nitrogen atoms was a pressure of 2×10^{-8} mm. The results showed that less than 10^{-3}% of the nitrogen atoms originally condensed could be recovered. It is concluded that although it is possible to stabilize appreciable concentrations of N atoms in a matrix (approximately 0.1%) the recovery of any appreciable number by evaporation of the matrix does not seem possible.

Herron, John T., J.L. Franklin, Paul Bradt, and Vernon H. Dibeler, "Kinetics of Nitrogen Atom Recombination", J. Chem. Phys., 30, 879-885, (1959).

The rate of recombination of nitrogen atoms in the nitrogen afterglow has been measured in a flow system using NO as a titrant and determining the NO content continuously by a mass spectrometer. From the nitrogen atom decay along a length of pyrex tube in a conventional flow system it was possible to measure the recombination rate in the presence of N_2, A, and He. Reference is made to the

research at McGill University where it was demonstrated that ground-state N atoms are a major constituent of active nitrogen, and also that some evidence exists that vibrationally excited N_2 molecules may be present, although there is some uncertaintly about their nature.

A brief discussion is given about the choice of a titrant, nitric oxide (NO) proved to be a simple and convenient one. The reaction is as follows, and

$$N + NO \rightarrow N_2 + O$$

has a rate constant greater than 5×10^{13} cm^3 $mole^{-1}$ sec^{-1}. The N atom concentration is given directly by the amount of NO consumed when the discharge is turned on. The titration was shown to be independent of the original NO concentration.

The experimental procedure is clearly described and an excellent discussion is given of the experimental results and kinetics of the recombination reaction.

$$N + N + M \xrightarrow{k_1} N_2 + M$$

$$1/(N_b) - 1/(N_a) = k_1 M(t_b - t_a)$$

where (N_a), (N_b), and t_a, t_b are the N atom concentrations and times at the two injection points and b, respectively.

Mean $k_1 (N_2)$ 273 to 453°K = $5.7 \pm 0.2 \times 10^{15}$ cm^6 $mole^{-2}$ sec^{-1} and mean k_1 (A) = $2.8 \pm 0.3 \times 10^{15}$ cm^6 $mole^{-2}$ sec^{-1}.

For the reaction $N + W \xrightarrow{k_2} 1/.2\ N_2 + W$, mean $k_2 = 0.09 \pm 0.3$ sec^{-1}.

Hertzberg, Martin, "Ion-Atom Interchange as an Important Source of Ionospheric Atomic Nitrogen", J. Geophys. Research, 64, 1106, (1959).

This is an abstract of a paper presented at the 40th annual meeting of the American Geophysical Union, Washington, D.C., 4-7 May 1959. Secondary reactions involving the positive ions O^+, O_2^+, and NO^+ with the neutral species O, N, and N_2, O_2, and NO are shown to be significant in determining the composition balance of the upper atmosphere. This is manifested (a) in converting atomic ions to molecular ions, and (b) in bringing about the dissociation of molecular nitrogen. Atomic nitrogen is considered to be a major neutral component of the F2 region. This conclusion is consistent with rocket measurements of ion composition below 250 km. A tentative curve for the degree of dissociation of molecular nitrogen as a function of altitude was presented. It is also pointed out that the observed N^+/O^+ ion ratios above 250 km indicate that atomic oxygen is preferentially ionized by Lyman continuum radiation from the solar chromosphere.

Hildebrandt, F.A., C.A. Barth, and F.B. Booth, "Atom Concentration Measurements Using Electron Paramagnetic Resonance" Progress Report No. 20-371, Jet Propulsion Lab., Cal. Tech., 6 August 1959.

This report describes a method for measuring the atom-concentration of $N(^4S)$ and $H(^2S)$ produced by microwave discharges in pure N_2 and H_2. The electron paramagnetic resonance spectrometer was calibrated by means of a standard 0.1-F $MnSO_4$ solution. The

results for atomic nitrogen were confirmed by titration with NO.

Nitrogen has a nuclear spin of one, three hyperfine lines, and a Lande f factor of 2 centered near 3320 gauss. The paramagnetic salt manganous sulfate ($MnSO_4$) was used as a standard. This salt has a nuclear spin 5/2 and a g factor of 2, where g is the Lande splitting factor for the electron. The EPR measurements for nitrogen atoms were verified by titration with nitric oxide as described by Kaufman and Kelso (1957 and 1958). The reaction is

$$N + NO \rightarrow N_2 + O$$

When the flow of NO is increased from zero to an equimolar concentration of n, the afterglow changes from the orange of pure nitrogen to the blue of NO and disappears at the end point. The blue color is due to the γ, β, and δ bands of NO which is produced by the reaction of the atomic oxygen formed in the above equation as follows

$$N + O + M \rightarrow NO + M + h\nu$$

A slight excess of NO produces a pale green afterglow from the reaction

$$NO + O \rightarrow NO_2 + h\nu$$

The apparatus and experimental technique of the EPR measurements are fully described in the report. Reproducible EPR measurements are within $\pm$ 5 per cent.

Holmes, Julian C. and Charles Y. Johnson, "Positive Ions in the Ionosphere", Astronautics, 4, 30-31, 102-105, (1959).

An excellent description is given of the mass analysis operations of the Bennett RF mass spectrometer adapted for rocket borne

application. A schematic diagram shows the essential components of the positive ion tube; the theory of the principles involved is discussed in full. Six positive ions were identified during the four rocket flights: masses 32^+, 30^+, 28^+, 18^+, 16^+, and 14^+. Of these six masses it was found that 32^+, 30^+, and 16^+ dominate the spectra. The large amount of mass 30^+ was a surprising and unpredicted feature of the distributions. The following ion-chemical charge exchange reaction is included to explain the presence of mass 30^+ which presumably is nitric oxide.

$$O^+ + N_2 \rightarrow NO^+ + N$$

Hunten, D.M., H.J. Koenig, and A. Vallance Jones, "Rotational Structure of the 3914 A N_2^+ Band in Sunlit Aurorae", Nature, 183, 453-454, (1959).

This is a report of striking sunlit auorae which were observed on the evening of 3 and 4 September 1958 from Saskatoon, Canada. A plate was obtained during each night with an f/0.8 Schmidt grating spectrograph. Unusually high relative intensities of the first negative N_2^+ bands for higher vibrational bands were recorded. The rotational temperature derived from the band by plotting log(I/K') against K'(K'+1) was 2100°K.

Two possible mechanisms are suggested to explain the high rotational temperature. (a) The N_2^+ ions might be in radiative equilibrium with the sunlight. (b) The N_2^+ ground-state might have a rotational distribution corresponding to thermal equilibrium at some high temperature which may or may not be the temperature of the atmosphere at the altitude concerned. The authors conclude

that the N_2^+ ions observed had a rotational temperature in the ground-state of 2100°K. Apparently there was no way of deciding whether this was the temperature of the atmosphere at the height observed.

Il'in, R.N., V.V. Afrosimov, and N.V. Fedorenko, (Translated by H. Lashinsky), "Ionization of Air by H^+ and H_2^+ Ions", J. Exptl. Theoret. Phys., (U.S.S.R.), 36, 41-48, (1959); Zhur. Eksptl. i Teoret. Fix., 36, 41-48, (1959).

The present investigation was undertaken to study ionization in single collisions of H^+ and H_2^+ ions with air molecules. The procedure consisted of passing a beam of primary H^+ and H_2^+ ions first through a monochrometer and then through a system of collimating slots into the collision chamber which contained air at a pressure of 1.5×10^{-4} mm Hg.

With reference to the nitrogen molecule the following mechanisms are given as those most probably leading to the formation of secondary ions.

$$H^+ + N_2 \rightarrow H^0 + N_2^+ \quad \text{(a)}$$

$$H^+ + N_2 \rightarrow H^+ + N_2^+ + e^- \quad \text{(b)}$$

$$H^+ + N_2 \rightarrow H^0 + N_2^{++} + e^- \quad \text{(c)}$$

$$H^+ + N_2 \rightarrow H^+ + N_2^{++} + 2e^- \quad \text{(d)}$$

It is stated that the N_2^+ ions formed by reactions (a) and (b) and the N_2^{++} ions which result from reactions (c) and (d) are predominantly stable. It is pointed out that the atomic particles N, N^+, and N^{++} are formed by the dissociation of the stable secondary

ions by various methods. Reference to Figure 7 in the paper shows that the number of N^+ and N^{++} atomic ions is less than 50 percent of the molecular N_2^+ ions. Thus the maximum number of unstable N_2^+ ions is less than one-third of the total number.

Jackson, J. L., "Dynamic Stability of Frozen Radicals. I. Description and Application of the Model", J. Chem. Phys., 31, 154-157, (1959).

The dynamic stability of a mixture containing free radicals is considered in the present paper. The purpose of the study was to obtain an expression for the critical concentration of free radicals. The model, calculation, and application are described. For nitrogen atoms in a nitrogen molecule lattice, the calculated critical concentration was of the order of magnitude of 0.3 percent.

Kaufman, F. and J. Kelso, "Reactions of Atomic Oxygen and Atomic Nitrogen with Oxides of Nitrogen", Seventh Symposium (International) on Combustion at London and Oxford, 28 August - 3 September 1958, published by Butterworths Scientific Publications, 53-56, (1959).

The experimental details and instrumentation are fully discussed. With reference to atomic nitrogen the reactions with nitric oxide, nitrogen dioxide, and nitrous oxide are considered. Similar to the use of NO_2 for titration of atomic oxygen because of its fast reaction, NO fulfills the same purpose for atomic nitrogen.

$$N + NO \rightarrow N_2 + O$$

The rate constant is given as between 10^{11} to 10^{12} cc mole^{-1} sec^{-1} and probably about 4×10^{12} cc mole^{-1} sec^{-1}. A discussion is given on color changes for this titration.

The reaction with NO_2 (nitrogen dioxide) is also extremely fast. The following reactions are all extremely fast, making it futile to inquire into the details of the overall mechanism

$$N + NO_2 \rightarrow N_2O + O$$

$$N + NO_2 \rightarrow 2\,NO$$

$$N + NO \rightarrow N_2 + O$$

$$O + NO_2 \rightarrow NO + O_2$$

In regard to the reaction with N_2O (nitrous oxide) the authors state that they found no reaction between N and N_2O, probably because of its potential violation of spin selection rules. However there is evidence that the vibrationally excited ground state of N_2 is present in active nitrogen and that N_2O is very efficient in bringing about its relaxation. The bimolecular reaction $N + N_2O \rightarrow N_2 + NO$ is stated to be at least 10^4 times slower than N + NO.

Khvostikov, I.A. and T.G. Megrelishvili, "New Bands and Lines in the Twilight Sky Spectrum", Nature, 183, 811, (1959).

The authors report that they have been making continuous observations of the twilight sky for 17 years with the objective of studying the features of the earth's atmosphere. These studies have been made at the Abastumai Astrophysical Observatory. In the present letter to the editor, it is reported that in addition to observing the bands of the first positive system of N_2, the authors

have found two bands of a system which they believed was not hitherto known. These were identical with the bands recently identified by LeBlanc, Tanaka, and Jursa [J. Chem. Phys., 28, 979, (1958)]. A list of the observed bands and lines is given in an extensive table together with the wavelengths, the band systems, and the atomic and molecular species.

Kurweg, U.H. and H.P. Broida, "Vibrational Intensity Distributions in the Nitrogen Afterglow", J. Molec. Spectros., 3, 388-404, (1959).

Nitrogen afterglows produced in a fast-flow system by an electrodeless discharge have been studied as a function of pressure, flow, dilutent, and temperature. The authors state that while a large number of theories have been proposed to account for the Lewis-Rayleigh afterglow, only the "atomic theory", satisfactorily accounts for the $N_2(^5\Sigma)$ molecule to be transferred into the $^3\Pi$ state from which the familiar $B\ ^3\Pi - A\ ^3\Sigma$ radiation eminates. The theory is also able to explain the absence of a 13th level and the strong population of the 10, 11, and 12th levels. The authors show that the vibrational intensity distributions are not explainable by the generally accepted preassociation model of the afterglow phenomena.

It is concluded that the reaction

$$N_2(^5\Sigma) + M \rightarrow N_2\,(B\ ^3\Pi) + M$$

where M is either an $N_2(^1\Sigma)$ molecule or a rare gas atom without modification would succeed in populating only the 12th vibrational level of the $B\ ^3\Pi$ state. To account for the observed 9, 10, and 11th level populations it is postulated that during the preassociation process (a) the body M removes the excess energy, (b) energetic

collisions are able to lower the $^5\Sigma - {}^3\Pi$ potential curve crossing point, or (c) rotational energy is conserved, thus resulting in the population of low vibrational levels in high rotational states. While the preassociation theory of the nitrogen afterglow is consistent with some of the properties of active nitrogen, it is is unable in its present form to account for the relative intensities of the vibrational bands of the N_2 first positive system.

Kvifte, G., "Nightglow Observations at Ås During the I. G. Y.", Geofys. Publikajoner Geophysca Norvegica, XX, No. 12, 14 pages, two plates, (1959).

A new grating spectrograph, built by grants from the Norwegian Research Council for Sciences and Humanities, was used during the IGY in the study of auroral and nightglow. Full technical data and photographs of the spectrograph are included in this report. The atomic nitrogen doublet at 5200 A appeared on the spectra of the nightglow and is shown in Plate I, No. 1. No auroral activity was visible on the nights when the nightglow spectra were taken. The author states that according to this knowledge the forbidden N II lines have not been observed in the nightglow by others. Of the eignt spectra taken from the region $\lambda\lambda$ 6250-6650 A, all shown in Plate II, six distinctly show the stronger component ($^3P_2$ - $^1D_2$) at 6583 A of the N II "doublet". There seemed to be a correlation between the intensities of the H_α line and the N II ($^3P_{2,1}$ - $^1D_2$) lines. An explanation is given for the absence of the line at 6548 A when 6583 A is present. The former is comparatively weak when compared to the latter.

Kvifte, G., "Auroral and Nightglow Observations at Ås, Norway", J. Atm. Terrest. Phys., 16, 252-258, (1959).

The author describes a new grating spectrograph that was constructed at the Department of Physics, Agricultural College of Norway for use in the study of the upper atmosphere. A summary is given of the results of auroral observations. The auroral spectrograms showed the N I forbidden doublet at 5200 A as relatively strong, but no other N I lines were observed between 5200 and 6650 A. The N II multiplet at 5660 to 5730 A with six components and the singlet line at 6482 A were present on all spectra. From January to April 1958 eleven successful nightglow spectrograms were taken. The most remarkable results obtained were observation of a sharp H_α line and the presence of the forbidden N II $({}^3P_{1,2} - {}^1D_2)$ lines. There seemed to be a close correlation between the intensities of the H_α lines and the N II forbidden lines.

Minkoff, G.J., F.I. Scherber, and J.S. Gallagher, "Energetic Species Trapped at 4.2°K from Gaseous Discharges", J. Chem. Phys., 30, 753-758, (1959).

Reference is made to the calorimetric technique developed by Broida and Lutes [J. Chem. Phys., 24, 484, (1956)] for estimating the abundance of trapped atoms. The present investigation had for its objective the reduction of the effect of several recognized sources of error in the calorimetric method. The calorimeter was heated rapidly to 40 - 50°K by a small heating coil. This had the advantage that less heat was required when atoms or radicals are present in the deposit.

Figure 1 in the paper is a diagram of the calorimeter employed, showing condensing regions, electrical leads, and helium heater. The concentration is deduced from the reduction in electrical energy needed to raise the calorimeter to some particular temperature. The temperature measurement and experimental procedure are described in detail.

It was observed that in this experiment nitrogen appeared to be dissociated to the extent of two percent in the frozen solid. The concentration of atoms in the solid would be double this value. It is stated that although the results are not final they do confirm the potential usefulness of the calorimetric approach to the study of free radicals. It is stated that to obtain unambiguous atomic concentrations, calorimetric findings may need critical analysis in terms of optical spectroscopy and ESR (electron spin resonance) measurements.

Moyer, James W. and Arnold M. Bass, "Free Radical Chemistry", Chem. Eng. News., 37, Aug. 24 Issue, 51-56, (1959).

This is a feature article briefly outlining the program of the study of Free Radical Research at the National Bureau of Standards, Washington, D.C. Four main features of the project are given. (a) The research was not aimed toward free radical utilization, but rather the primary objective was toward obtaining basic data and exploring original approaches. (b) According to Dr. Broida, the project director, there was a need for original ideas and ingenious methods, with freedom of choice given to the participating scientists to devote their entire efforts to research. Each of the selected scientists of proved ability was permitted to progress following

their own initiative. (c) The third feature was that of joint government-industry participation. A list of the industrial participants in the NBS Free Radical Research Program is included. (d) The fourth feature of the project related to communications, one of the chief aims being dissemination of the information obtained.

Brief mention is made that nitrogen atoms could be produced in an electric discharge and subsequently trapped in a solid condensate at the temperature of liquid helium (4.2°K). Electron spin resonance studies demonstrated the existence of nitrogen atoms in the condensed solid. The stability of the trapped atoms and radicals was studied. In the case of nitrogen atoms in a molecular matrix at 4.2°K no change in the ESR (electron spin resonance) was observed in 24 hours. It was also shown that nitrogen atoms could be stored in the matrix and then transferred from one cold surface to another without loss of active species. A bibliography of twelve selected references is included.

Nesmeyanov, Alexander, "Soviets Measure Geomagnetic Field", Aviation Week, 71, No. 7,63-65, (1959).

This is a news item reporting that the Soviet Union had disclosed some results of its satellite and rocket program at the International Cosmic Ray Conference. The report was given in March, 1959 to the USSR Academy of Sciences by Alexander Nesmeyanov, the President. A summary was published in Soviet newspapers.

With reference to atmospheric composition in the high atmosphere it was revealed that Soviet research had established the presence

of ions of mass number 16 which predominate at altitudes from 226 to 1000 km. Atomic oxygen constituted the basic gaseous component within the altitude range 226 to at least 800 km. Atomic nitrogen was also detected as well as heavier particles of masses 28 N_2 and 30 NO. It was found that the atomic nitrogen content in relation to atomic oxygen ranged from 1 to 10% depending upon altitude, geographic latitude, and lapse of time. Definite dependence of all components of the ionosphere on geographic latitude was established.

Nesmeyanov, A.N., "Information on Soviet Bloc International Geophysical Cooperation-(1959)", #PB131632-79, U.S. Department of Commerce, Office of Technical Services, 14 August 1959.

This publication is a complete translation of a newspaper article which surveys USSR activities in space exploration. The table of contents are:

I. General

II. Rockets and Artifical Earth Satellites

III. Upper Atmosphere

IV. Gravimetry

V. Oceanography

VI. Arctic and Antarctic

With reference to atomic nitrogen it is stated that a mass spectrometer was installed on the third Russian satellite in order to obtain a large number of mass spectra of the positive ions which characterize the chemical composition of the ionosphere at altitudes of 226 to 1000 km.

It was found that ions of mass number 16 (atomic oxygen) predominate from an altitude of 226 to 1000 km. Ions of atomic nitrogen were also recorded in addition to the ions of atomic oxygen. Ions of mass 28 and mass 30 were also observed. The latter, mass 30 nitric oxide, was recorded up to altitudes of 350 km. The relative concentration of atomic nitrogen with respect to atomic oxygen changes from 1 to 10% depending on the altitude, geographic latitude, and time. The relative concentration of nitric oxide ions and molecular nitrogen was found to drop sharply with an increas in altitude. The number of NO ions at an altitude of 230 km was found to be 25 to 40% with respect to atomic oxygen.

Nicolet, M., "La Thermosphere", Ann. geophys., 15, 1-22, (1959).

In this discussion the author has assumed the following relationship at 110 km and above that height. All constituents are assumed to be in diffusive equilibrium.

$$n(O) = 1/2\ n(N_2)$$

With reference to atomic nitrogen and the dissociation of molecular nitrogen, the author shows that nitric oxide (NO) and atomic nitrogen are inter-related. As a result, atomic nitrogen remains a minor constituent and does not affect the atmospheric mean molecular mass. These inter-relationships are given as follows:

$$O + N + M \rightarrow NO + M$$

$$NO + N \rightarrow N_2 + O$$

$$N + O_2 \rightarrow NO + O$$

$$n(NO) = 0.1\ n(O_2) \times e^{-4200/RT}$$

$$N_2^+ + e^- \rightarrow N + N$$

$$N_2 + h\nu \rightarrow N_2^+$$

$$O^+ + N_2 \rightarrow NO^+ \quad N$$

Nicolet, M., "The Constitution and Composition of the Upper Atmosphere", Proc. IRE, 47, 142-147, (1959).

Nicolet in the present article has given a general survey of observations and theoretical possibilities of the constitution and composition of the upper atmosphere. The topics considered are: (a) the description of the atmosphere, (b) interrelations between pressure, temperature, and density, (c) the composition of the homosphere, (d) dissociation of molecular oxygen, (e) dissociation of molecular nitrogen, (f) diffusion in the thermosphere, and (g) the conduction of heat.

The effect of dissociative recombination of N_2^+ (or the ion-atom interchange collision) is considered as a mechanism for the continuous production of atomic nitrogen. Molecular nitrogen ions are produced by the action of X-rays and ultraviolet radiation. Reference is made to the short lifetime of N_2^+ ions in the F region. The following processes are given for the rapid loss of molecular nitrogen ions.

$$N_2^+ + e^- \rightarrow N + N$$

$$N_2^+ + O \rightarrow NO^+ + N$$

The atomic nitrogen may react with molecular oxygen

$$N + O_2 \rightarrow NO + O$$

and subsequently with nitric oxide

$$NO + N \rightarrow N_2 + O$$

The production of atomic nitrogen by the ion-atom interchange

collision is shown as follows:

$$O^+ + N_2 \rightarrow NO^+ + N$$

$$O^+ + O_2 \rightarrow O_2^+ + O$$

The author states that the maximum concentration of atomic nitrogen in the F region would be of the same order as that of $n(O_2)$ between 150 and 180 km. The lifetime of a nitrogen atom is considered to vary with altitude, there is also a daily variation.

-Nicolet, Marcel, "Constitution of the Atmosphere at Ionospheric Levels", J.Geophys. Research, 64, 2092-2101, (1959).

This paper was presented before the International Symposium on Fluid Mechanics in the Ionosphere, 9-15 July 1959, Cornell University, New York, With reference to the production of atomic nitrogen in the ionosphere the following mechanisms and reactions are given.

The predissociation mechanism has a rate coefficient of the order of 10^{-12} sec^{-1}. It is therefore a very slow process and cannot lead to important dissociation. However ionization followed by dissociative recombination $N_2^+ + e^- \rightarrow N + N$ must be considered an important process since N_2 can be ionized by ultraviolet light and x-rays in the various ionospheric regions.

The ion-atom interchange represented by the following equations is also considered a source of atomic nitrogen.

$$O^+ + N_2 \rightarrow NO^+ + N + 1 \text{ ev}$$

$$N_2^+ + O \rightarrow NO^+ + N + 2 \text{ ev}$$

When a nitrogen atom is produced it reacts with molecular oxygen

$$N + O_2 \rightarrow NO + O$$
(coefficient a_1)

which has an activation energy of about 6 kcal. Atomic nitrogen also reacts nitric oxide,

$$NO + N \rightarrow N_2 + O$$

the activation energy being very small, less than 0.5 kcal.

The author states that the concentration of atomic nitrogen depends on molecular nitrogen and atomic oxygen, and in order to determine the concentration of atomic nitrogen it is necessary to know the exact ionization rates of molecular nitrogen and atomic oxygen in the whole thermosphere. The concentration is expressed by

$$n(N) = \frac{n(N_2)\ I_{N_2} + n(O)I_o}{a_1\ n(O_2)}$$

where I_{N_2} and I_o denote the ionization rates of molecular nitrogen and atomic oxygen, respectively. It is further pointed out that the lifetime τ_N of a nitrogen atom is defined by

$$\tau_N = 0.7/[2a_1 n(O_2)]$$

which varies with height. The lifetime may be sufficiently long in the F_2 layer to permit diffusion to be effective. It is concluded that the concentration of atomic nitrogen cannot remain constant in the upper levels of the thermosphere because of the varying boundary conditions in the F_1 layer. The concentration of atomic nitrogen n(N) will also be subject to variations associated with solar activity.

Ogawa, M. and Y. Tanaka, "New Emission Bands of N_2 in the

Vacuum Ultraviolet Region", J. Chem. Phys., 30, 1354-1355, (1959).

The authors report the observation of six new bands of nitrogen in the spectral region between 1600 and 2050 A. The Lyman-Birge-Hopfield bands ($a\ ^1\Pi_g$ - $X\ ^1\Sigma_g^+$) also appeared in the same region; however, some of the bands were obscured by their higher rotation lines. This obscurity was removed when the tube was coated in liquid nitrogen.

The wavelengths and wave numbers of the new emission bands of nitrogen are tabulated in Table I of the paper. The upper state of the present emission bands was considered to be probably the $a'\ ^1\Sigma_u^-$ (v = O).

Oldenberg, O., "A Short Duration Afterglow of Nitrogen; Survey of Afterglows", Planetary, Space Sci., 1, 40-42, (1959).

Attention is called to a new type of nitrogen afterglow which has a shorter duration than the well established types. When low pressure 3×10^{-13} mm Hg nitrogen is transversed by a beam of electrons it is surrounded by a diffuse glow emitting the first positive bands. This is interpreted as an afterglow. Professor Oldenberg attributes the process to be due to metastable nitrogen molecules, $a\ ^1\Pi_5$, and to be different from the Lewis-Rayleigh afterglow (excitation of $^5\Sigma$, energy transfer to $B\ ^3\Pi$). The metastable $a\ ^1\Pi$ molecules diffuse out of the space occupied by the beam and are thrown by collision into the unstable $B\ ^3\Pi$ state and then emit the first positive bands. The time for the diffusion is given to be about 5×10^{-5} sec.

The author compares this afterglow with four other types.

(a) The Lewis-Rayleigh afterglow which is distinguished by its long duration and which receives its energy from recombining normal nitrogen atoms.

(b) The afterglow investigated by Noxon [Ph.D. Thesis, Howard University, (1957)].

(c) Kaplan's auroral afterglow.

(d) The recombination of ions and electrons, which produces an afterglow whose spectrum is similar to the auroral afterglow and which takes place within milliseconds after a discharge.

(e) The Thompson-Williams afterglow discussed in the present paper. It is of short duration and due to the diffusion of metastable molecules (a $^1\Pi$) from the electron beam and later conversion to the B $^3\Pi$ level.

Peyron, M., E.M. Horl, H.W. Brown, and H.P. Broida, "Spectroscopic Evidence for Triatomic Nitrogen in Solids at Very Low Temperature", J. Chem. Phys., 30, 1304-1310, (1959).

The authors report that from the considerable spectral data obtained from the glow emitted by solid nitrogen near 4^oK some of the spectrum could be attributed to a weakly bound triatomic molecule, N_2-N. It is pointed out that the three lowest electronic levels of atomic nitrogen, ^2P, ^2D, and ^4S are involved in the 8 line groups which were found. An energy level diagram for the 8 observed line groups is shown in Figure 6 of the paper. Evidence was also obtained for the existence of an N_2-O molecule similar to the N_2-N.

Porter, George, "Recent Progress in Free-Radical Spectroscopy",

Spectrochim. Acta, 14, 261-270, (1959).

This paper was presented before the conference on molecular spectroscopy held in London, 27-28 February 1958. The author has reviewed the new techniques for study of the spectra of free radicals and unstable molecules. These include flash photolysis, matrix isolation methods, and paramagnetic resonance.

Brief reference is made in the present paper to the free radical stabilization by Broida and Pellam [Phys. Rev., 95, 845, (1954)]. The method involved the formation of free radicals in a gas phase flow system by thermal or electrical dissociation and the mixture of products subsequently condensed or "trapped" on a cold surface. The use of liquid helium for the purpose of isolating and trapping radicals is mentioned. This method is applied to obtaining atomic nitrogen.

Price, W.C., "Spectroscopy in the Vacuum Ultraviolet", Advances in Spectroscopy, Vol. I, pp. 56-75, edited by H.W. Thompson, Intersciences Publishers, Inc., New York, (1959).

This is an excellent review of spectroscopy in the vacuum ultraviolet. The contents of this chapter are as follows.

I. Introduction

II. Experimental technique

A. Sources of radiation

B. Spectrographs

C. Detectors

D. Wavelength standards

III. Atomic spectroscopy

A. Autoionization

B. Photoionization cross-sections

C. High resolution studies

D. Analysis

IV. Molecular spectr ›py

A. Diatomic molecules

B. Polyatomic molecules

C. Absorption coefficients

D. Photoionization measurements

V. Miscellaneous topics

References

VI. Addendum

A bibliography of 72 references is given. Many of these refe. to work done at the Geophysics Research Directorate of the Air Force Cambridge Research Center by Watanabe and co-workers and by Tanaka and his collaborators.

Rees, M.H., "Absolute Photometry of the Aurora - I. The Ionized Molecular Nitrogen Emission and the Oxygen Green Line in the Dark Atmosphere", J. Atm. Terres. Phys., 14, 325-337, (1959).

A low latitude aurora was measured photometrically. Three prominent emission features, $\lambda 3914$ band of the first negative group N_2^+, $\lambda 5577$ of O I and $\lambda 6300$-6364 of O I, were isolated with narrow pass band filters and recorded continuously throughout the night in the meridian sweep. The absolute emission intensity for $\lambda\lambda 3914$ and 5577 A is given at a selected zenith distance. The ratio of instantaneous intensities I(O) 5577 to I(O) 3914 was found to be

essentially constant over an intensity range of three powers of ten and to be independent of the type of auroral form.

For 100 eV electrons, the cross-section is 2.87×10^{-16} cm^2 for ionization of N_2 by electron impact. Reference is made to Stewart [Proc. Phys. Soc., (London), A69, 437, (1956)] who had measured the probability of excitation of the (o, o) negative band of N_2^+. From the published curves a cross-section of 6.2×10^{-18} cm^2 for 100 eV electrons was obtained.

From data given by Meinel (1952), Bates (1955), and Seaton (1954) the primary mechanism resulting in the negative group N_2^+ band system is $N_2 + X \rightarrow N_2^{+\prime} + X + e^-$ where X represents the energetic particle and $N_2^{+\prime}$ is the ionized nitrogen in the excited state. The above reaction is followed by

$$N_2^{+\prime} \rightarrow N_2^+ + h\nu \quad (\lambda\lambda 3914)$$

giving rise to the first negative system, and ionic recombination with negative oxygen ions,

$$N_2^+ + O^- \rightarrow N_2 + O(^1S)$$

yielding the upper state of O I from which the desired emission is obtained.

$$O(^1S) \rightarrow O(^1D) + h\nu \quad (\lambda\lambda 5577)$$

The above reactions indicate a constant ratio and satisfy this aspect of the experimental results.

Rees, M.H., "Absolute Photometry of the Aurora - II. Molecular Nitrogen Emission in the Sunlit Atmosphere", J. Atm. Terrest. Phys., 14, 338-344, (1959).

The absolute emission intensity of a sunlit aurora was determined

for the first negative group $\lambda 3914$ band of N_2^+ by subtracting the emission intensity in the dark atmosphere from the total measured intensity. The method is based on the constancy of the ratio of emission intensity of the oxygen green line O I $\lambda 5577$ to the $\lambda 3914$ emission in the dark atmosphere. The ion density of N_2^+ was computed as a function of height from the emission rate per unit volume.

The following two possible excitation mechanisms are given to explain the first negative group N_2^+ emissions from an atmospheric region illuminated by sunlight.

$$N_2(X\ ^2\Sigma_g^+) + h\nu\ (<660\ \text{Å}) \rightarrow N_2^+\ (B\ ^2\Sigma_u^+) + e^-$$

There is simultaneous photo-ionization and excitation to the required electronic level, followed by resonance scattering.

$$N_2^+(X\ ^2\Sigma_g^+) + h\nu\ (<3914\ \text{Å}) \rightarrow N_2^+\ (B\ ^2\Sigma_u^+)$$

For resonance excitation the photon emission is given by

$$\pi_r = P_{3914}\ [N_2^+]$$

where P_{3914} is the $\lambda 3914$ photon emission probability per illuminated ion per sec and $[N_2^+]$ represents the number of N_2^+ ions per cm^3. The value of P is 0.3 sec^{-1}. The N_2^+ ion concentration was calculated for different altitudes.

Height km	$[N_2^+]$ (ion-cm^{-3})
600	446
500	1000
400	2136
300	4000
200	8400

Rice, O.K., "The Recombination of Atoms and Other Energy-Exchange Reactions", IXth International Astronautical Congress, Amsterdam, 1958, Springer-Verlag-Wien, pp. 9-19, (1959).

A discussion is given of the recombination of atoms and the dissociation of a diatomic molecule in the presence of a third body. In regard to nitrogen atoms the reaction

$$2\,N + M \rightarrow N_2{}^* + M$$

is given where M is usually N_2 and $N_2{}^*$ is the excited species which produces the spectrum. The rate constant for this association reaction is 0.2×10^{-32} ml^2 $molecules^{-2}$ sec^{-1}, which was estimated by Berkowitz, Chupka, and Kistiakowsky [J. Chem. Phys., 25, 457, (1956)]. The following mechanism is believed to occur.

$$N + N + M \rightleftharpoons N_2(^5\Sigma_g^+) + M$$

$$N_2(^5\Sigma_g^+) + M \rightarrow N_2(B\,^3\Pi_g) + M$$

The $B\,^3\Pi_g$ state emits radiation in falling to the $A\,^3\Sigma_u^+$ state. A brief discussion is given of the rate constants of the above reations.

Schulze, Helga, "Afterglow of Nitrogen at Atmospheric Pressure", Z. Physik Chem., 210, 176-195, (1959).

A blue afterglow was observed at atmospheric pressure and a temperature of about $1500^\circ K$ in a stream of nitrogen behind an electric arc discharge. The duration of the afterglow was about 10^{-3} seconds. The intensity of the afterglow decreased with increasing amounts of nitrogen.

Photographs of the spectra, a table of assignments of the band systems, and a potential energy curve after Reinecke [Z. Physik, 135, 361-375, (1953)] are included in the paper. An extended theoretical discussion is given of the mechanism and recombination of nitrogen atoms.

Seaton, M.J., "Electron Impact Ionization of Ne, O, and N", Phys. Rev., 113, 814, (1959).

The author has used the Bethe approximation to determine the calculated cross sections for ionization of Ne, atomic oxygen, and atomic nitrogen. The approximation of Bethe is

$$Q(E) = \frac{I_H}{\pi \alpha E} \int_0^{E - I} \frac{a(W)}{I + W} \ln \left(\frac{4 E \tau}{I + W} \right) dW$$

where Q(E) is the total cross section for ionization of an atom by electrons of kinetic energy E, and a(W) is the cross section of photoionization, W is the energy of the ejected electron, I is the threshold ionization energy, I_H is the threshold energy of hydrogen, α is the fine structure constant, and τ is a constant of order unity.

Figure 1 in the paper shows the experimental cross section Q_{Ne} and the calculated cross sections Q_O and Q_N.

Stacey, F.D., "The Possible Occurrence of Negative Nitrogen Ions in the Atmosphere", J. Geophys. Research, 64, 979-981, (1959).

The question of the existence of negative ions of molecular and atomic nitrogen is considered. It is stated that liquid conduction counter experiments give evidence of N_2^-, and as a result the

possibility for their occurrence in the atmosphere cannot be discounted. For experimental evidence the observations of Davidson and Larsh [Phys. Rev., 77, 706, (1950)] are discussed. Pulses of electrical conduction were observed to occur in an ionization chamber in which the ionized media were dilute solutions of nitrogen and oxygen in liquid argon. They concluded that N_2^- ions were formed and that N_2 has an electron affinity.

The estimated cross section for capture of electrons by N_2 is given

$$Q \sim 2 \times 10^{-19} \text{ cm}^2$$

This estimate was obtained from measurements made with an applied electric field and therefore is not necessarily appropriate to electrons at 90° K. The following mechanism is discussed.

$$N_2 + e^- \rightleftarrows N_2^-$$

$$N_2^- + N_2^+ \rightarrow 2N_2$$

The rocket experiment by Johnson and Heppner [Trans. Am. Geophys. Union, 37, 350, (1956)] is considered as possible direct evidence for existence of negative nitrogen ions. Negative ions with masses 46, 32, 29, 22, and 16 were observed. The author of the present paper points out that even though masses 14 and 28 were not recorded, there is the possibility that mass 29 could be N_2^- with nitrogen isotopes of masses 14 and 15, while mass 22 might be an isotope of neon.

It is concluded that N_2^- may not be a major constituent of the F_2 layer; yet from estimates as a minor constituent it could have a significant influence.

Stacey, F. D., "Author's Reply to the Preceding Discussion", J. Geophys. Research, 64, 2470, (1959).

This is a reply to the discussions by Bates [J. Geophys. Research, 64, 2469, (1959)]. The author concludes that until more certain experimental evidence is available the existence of N_2^- ions is an open question. Criticism is made of the assumption that ϵ is taken to be zero in Bate's discussion. Stacey in the present reply notes that it is very difficult to make decisive experiments because of the expected very short life of N_2^-. The possibility of using electron mobility measurements as in liquid oxygen is suggested.

Tanaka, Y., F. LeBlanc, and A. Jursa, "Second Positive Bands in the Lewis-Rayleigh Afterglow of Nitrogen", J. Chem. Phys., 30, 1624-1625, (1959).

Reference is made to the observance of the second positive bands of nitrogen by Kaplan (1932, 1934, 1937, 1938) and also by Herman and Kenty [Nature, 161, 1018, (1948); J. Chem. Phys., 23, 1555, (1955)]. The authors state that these are specific types of afterglow and that no report has been made of an observation of the second positive bands in the Lewis-Rayleigh afterglow of nitrogen.

The bands were not observed at room temperature but were observed when the glow was cooled with liquid nitrogen. The intensity of the bands was almost as strong as the first positive bands.

The authors propose an inverse homogeneous predissociation for the process

$$N(^4S) + N(^2D) \rightarrow N_2 (C\ ^3\Pi_u)\ v = 4$$

$$N_2 (C\ ^3\Pi_u) \rightarrow N_2\ B(^3\Pi_g) + h\nu \text{ (second positive bands)}$$

Tanaka, Y., A.S. Jursa, F.J. LeBlanc, and E.C. Y. Inn, "Spectroscopic Study of the Afterglows of N_2 and $(N_2 + O_2)$ in the Vacuum Region", Planetary Space Sci., 1, 7-13, (1959).

This is a study of the relationship between the partial pressures of N_2 and O_2 for each of the four distinct stages of the nitrogen afterglow when the partial pressure of O_2 in a mixture of N_2 and O_2 is changed. Three groups of N I lines at λλ1200, 1493, and 1743 A were selected for the measurement of the concentration of the N-atom in $2p^3\ ^4S$, $2p^3\ ^2D$, and $2p^3\ ^2p$. The concentration measurement was carried out by means of photographic photometry using SWR plates and these lines as background.

There are four stages of the nitrogen afterglow which can be produced simply by changing the partial pressure of O_2. These four stages are straw-yellow (Lewis-Rayleigh afterglow), blue-glow, dark (no glow), and greenish-gray, In Table 1 of the paper an excelient summary is given of the observed emission spectra, the absorption spectra, and the proposed reactions for each glow stage. The absorption spectra of these glows in the vacuum region showed the presence of atomic nitrogen, atomic oxygen, and nitric oxide.

The concentrations of $N(^4S)$ in the first stages of the afterglow are shown in Table 3 of the paper. Figure 2 is a photograph of the absorption spectra of the first stage, and the absorption bands of the blue afterglow are shown in Figure 3. The bibliography contains

19 references to previous papers on the nitrogen-oxygen afterglow.

Vanderslice, Joseph T., Edward A. Mason, and Ellis R. Lippencott, "Interactions Between Ground-State Nitrogen Atoms and Molecules. The N-N, $N-N_2$, and N_2-N_2 Interactions", J. Chem. Phys., 30, 129-136, (1959).

One of the interests suggested for this study is the active nitrogen problem and various upper atmospheric phenomena. Potential energy curves for N-N interactions corresponding to the following states of N_2 were calculated: X $^1\Sigma_g^+$, A $^3\Sigma_u^+$, $^5\Sigma_u^+$, $^7\Sigma_u^+$, B $^3\Pi_g$, C $^3\Pi_u$, and a $^1\Pi_g$. These potential energy curves are summarized in Figure 2 of the paper which show the results to be consistent.

Vanderslice, Joseph T., Edward A. Mason, and William G. Maisch, "Interactions Between Oxygen and Nitrogen : O-N, $O-N_2$, and O_2-N_2", J. Chem. Phys., 31, 738-746, (1959).

The authors state that the interactions among oxygen and nitrogen atoms are of interest in connection with the calculation of the transport properties of air at very high temperatures and also with the interpretation of various upper atmospheric phenomena. Reference is made to the former paper by these authors [J. Chem. Phys., 30, 129, (1959)] in which potential energy curves for interactions between ground-state nitrogen atoms and molecules were reported. It is stated that when a ground-state oxygen atom (^3P) and a ground-state nitrogen atom (^4S) approach each other, six different interactions are possible, corresponding to the spectrosoopic states of the NO molecule:

$^2\Sigma$, $^2\Pi$, $^4\Sigma$, $^4\Pi$, $^6\Sigma$, and $^6\Pi$.

The following topics are discussed in the present paper: (a) bound states of NO, (b) $^4\Pi$ state of NO, (c) relations among the states of NO, (d) discussion of NO states, (e) O-N_2 and O_2-N_2 interations.

Varney, Robert N., "Molecular Ions", J. Chem. Phys., 31, 1314-1316, (1959).

This report discusses the physico-chemical analysis of data concerning drift velocities of ions in nitrogen. The present study reveals that N_4^+ ions are the stable ones at low temperature and E/p_o (the ratio of electric field strength to pressure). At higher temperature, or low pressure, and higher E/p_o the N_4^+ ions dissociate into N_2^+ and N_2.

This dissociation was found to behave identically with thermal dissociation of molecular gases. The following numerical data were obtained.

N_4^+ binding energy against dissociation into N_2^+ and N_2 = 0.50 ev.

Ion temperature in ^oK as a function of E/p_o in volts per cm per mm Hg is $\theta = 12.5\ E/p_o$.

Weissler, G. L., J. A. R. Samson, M. Ogawa, and G. R. Cook, "photoionization Analysis by Mass Spectroscopy", J. Opt. Soc. Am., 49, 338-349, (1959).

The experimental technique reported in the present paper is

essentially the same as reported by Hurzeler, Inghram, and Morrison [J. Chem. Phys., 28, 76-82, (1958)]. However there were two important differences: the monochromator was used with a light source with a good distribution of intense emission lines; and there was no window in the optical path between the monochromator exit slot and the mass spectrometer. There is a detailed description of the apparatus and experimental procedure.

Two different gases were used in the light source to obtain the ionization curves for N_2^+: an air-helium mixture and argon. The ionization potential of N_2 was found to be 15.6 ± 0.1 ev (795.5 ± 5 A). The appearance potentials of N_2^+ obtained by different methods are given in Table V.

Electronic state	Spectroscopic ionization potential ev	Electron impact ionization potential ev	Photon impact appearance potential ev
$N_2^+ \; X \; ^2\Sigma_g^-$	15.576	15.63	15.6 ± 0.1
$A \; ^2\Pi_u$	16.71	16.83	16.9 ± 0.3
$B \; ^2\Sigma_u^+$	18.748	18.76	18.8 ± 0.4
$C \; ^2\Sigma_u^+$	23.581	23.53	20.7 ± 0.4

The appearance potential of N^+ from dissociative ionization of N_2 is shown in Table VI of the paper.

Process and Products	$D(N_2)$ ev	Minimum energy ev	Photon impact A.P. (ev)
$N_2 \; X \; ^1\Sigma_g^+ \rightarrow N^+(^3P) + N(^4S)$	9.76	24.3	24.3 ± 0.2
$N^+(^3P) + N^*(^2D)$	7.37	24.3	

The authors conclude that the one appearance potential (A.P.) given in Table VI is not sufficient to choose between the two controversial values of the dissociation energy of nitrogen.

Wilkinson, P.G., "Forbidden Band Systems in Nitrogen. I. The Vegard-Kaplan System in Absorption", J. Chem. Phys., 30. 773-776, (1959).

The author reports that two bands belonging to the Vegard-Kaplan system ($A\ ^3\Sigma_u^+ - X\ ^1\Sigma_g^+$) of nitrogen were discovered. The 6-0 and 7-0 bands were observed in paths of 13 and 9 meter-atmospheres at high resolution. The spectrograph used in this investigation was a 21-foot vacuum Eagle spectrograph employing a 3x5-inch Bausch and Lomb concave diffraction grating (30,000 grannes per inch). The light source was a new xenon-light source for the vacuum ultraviolet described by Wilkinson and Tanaka [J. Opt. Soc. Am., 45, 344-349, (1955)].

Two other forbidden transitions of nitrogen are also reported in the present paper. These are the $a'\ ^1\Sigma_u^- \rightarrow X\ ^1\Sigma_g^+$ and probably the $^3\Delta_u \rightarrow X\ ^1\Sigma_g^+$. Reference is made to the observance of the Vegard-Kaplan bands in the spectrum of the night sky, and, though weak, in the spectra of auroras.

Wilkinson, P.G. and R.S. Mulliken, "Forbidden Band Systems in Nitrogen. II, The $a'\ ^1\Sigma_u^- \leftarrow X\ ^1\Sigma_g^+$ System in Absorption", J. Chem. Phys., 31, 674-679, (1959), (1959).

In the introductory portion of this paper the following known forbidden systems in nitrogen are listed: the Vegard-Kaplan bands

$(A\ ^3\Sigma_u^+ \rightarrow {}^1\Sigma_g^+)$; the Lyman-Birge-Hopfield bands $(a\ ^1\Pi_g \rightarrow X\ ^1\Sigma_g^+)$; the $C\ ^3\Pi_u \rightarrow X\ ^1\Sigma_g^+$ system; the $a'\ ^1\Sigma_u^- \rightarrow X\ ^1\Sigma_g^+$ system reported in the present paper; and a new system, $B'\ ^3\Sigma_u^- \rightarrow X\ ^1\Sigma_g^+$. The following topics in the paper are fully discussed.

I. Experimental: (a) Spectrograph, (b) Light Source, (c) Experimental procedure and wavelength stands, and (d) Gas purity.

II. Results.

III. Rotational intensity distributions.

IV. The Nature of the predissociation in state $Y\ ^1\Pi_g$ and the energy of dissociation of nitrogen.

V. Transition probabilities and mean lifetimes.

In regard to the energy of dissociation of molecular nitrogen it is stated that the value $D_o(N_2) = 9.756$ ev is pretty well established by thermal, spectroscopic, shock and detonation, and electron impact measurements. Serious difficulties of interpretation would arise if $D_2(N_2) = 7.373$ ev.

The authors state that the separate nitrogen atoms $^4S + {}^4S$ can give rise to the following molecular states: $^1\Sigma_g^+$, $^3\Sigma_u^+$, $^5\Sigma_g^+$, $^5\Sigma_u^+$, and the first of these is the ground state $X\ ^1\Sigma_g^+$; the second has been identified with $A\ ^3\Sigma_u^+$. If $D_o(N_2) = 7.373$ ev then $A\ ^3\Sigma_u^+$ (unless it first goes through a potential hill) could not dissociate into normal atoms since vibrational levels of this state are known well above 7.373 ev.

1960

Bates, D.R. and M. Nicolet, "Ion-Atom Interchange", J. Atmos. Terrest. Phys., 18, 65-70, (1960).

Attention is called to the importance of ion-atom interchange

$$X^+ + YZ \rightarrow XY^+ + Z$$

in the upper atmosphere as discussed by Bates [Proc. Phys. Soc., (London), A 68, 344, (1955)]. The rate coefficient was considered likely to be quite large in many instances because such an interchange does not require an electronic transition. Theoretical calculations give a value for the rate coefficient for any exothermic ion-atom interchange process between simple systems composed of only the main atmospheric constituents as large as 1×10^{-9} cm^3 sec^{-1}. The following reactions

$$O^+ + N_2 \rightarrow NO^+ + N + 1.0_9 \text{ ev}$$

$$O^+ + O_2 \rightarrow O_2^+ + O + 1.5_3 \text{ ev}$$

$$O^+ + NO \rightarrow O_2^+ + N + 0.1_6 \text{ ev}$$

are given and reference is made to Herzberg [J. Geophys. Research, 63, 856, (1958)]. By equating the rate at which O^+ ions are destroyed by the first two reactions to the inverse of the third which was believed to have no reaction energy Herzberg, using the data of Johnson, Meadows, and Holmes [J. Geophys. Research, 63, 443, (1958)], found that dissociation of nitrogen in the F-region was very high. The high degree of dissociation was attributed to the first mechanism which was considered to be a more important source of odd nitrogen atoms than the dissociative recombination reaction

$$N_2^+ + e^- \rightarrow N' + N''$$

In the present paper Bates and Nicolet consider the above reasoning to be incorrect since the reaction

$$O^+ + NO \rightarrow NO^+ + O + 4.3_6 \text{ ev}$$

causes the permanent loss of O^+ ions; NO^+ ions are considered to be the sole species of positive ion. It is concluded that the ion-atom

interchange does not exercise an appreciable direct influence on the degree of dissociation of nitrogen.

Blackwell, D.E., M.F. Ingham, and H.N. Rundle, "The Night-Sky Spectrum λλ 5000-6500 A", Astrophys. J., 131, 15-24, (1960).

A description is given of the spectrum of the night sky obtained at the cosmic-ray station of Chacaltaya (latitude 16°, height 17100 feet) at zenith distance 84°, using a dispersion of 78 A/mm. In the region λλ 5577-6500 A fifty-one OH emission lines were observed and identified.

With reference to the nitrogen emission line NI at 5199 A, the author states that the existence of this line in the night sky spectrum is usually considered doubtful. However in the present investigation, the authors demonstrate the existence of this line without any doubt. In Figure 4 of the paper a microphotometer record of the night sky spectrum in the region of the 5199 A shows the N I line. The intensity showed a maximum at 95 kilometers, a height which was considered too great for the OH emission. The intensity of the N I line (reduced to the zenith) was observed to be 1.8 rayleighs on both June 17/18 and August 8, 1958.

Broida, H.P. and R.W. Nicholls, "Phosphorescence of Nitrogen and Nitrogen-Argon Deposited Films at 4.2°K", J. Chem. Phys., 32, 623-624, (1960).

The purpose of this study was to investigate the possibility of inducing phosphorescence in the nitrogen deposited in films at

$4.2^{O}K$ by irradiation with a variety of light sources and to discover the spectral character of the phosphorescent light. The following four light sources were employed: an intense medium-pressure mercury arc lamp, a low-pressure mercury arc lamp, a 100 w projection lamp, and an iron arc.

A series of spectroscopic observations were made upon the phosphorescence produced in the films. It is reported that in all cases the spectrum during deposition showed the α, α', and β features of N I and O I and of the B.

It was concluded that the spectrum of the phosphorescence α, α', and β features was a restimulation of the afterglow conditions under which nitrogen atoms emit α and α'. It thus appears that light over the wavelength range 2000A to greater than 10,000 A produces a phosphorescence in atomic nitrogen - molecular nitrogen and atomic nitrogen-argon deposits which is a restimulation of the familiar afterglow.

Bromer, Herbert Heinrich, "Untersuchung des Auroral Afterglow und seiner Praparationsstadien. II Das Abklingen des Nachleuchtens im Airglow - NO - und Lewis-Rayleigh -Stadium", Z. Physik, 158, 1-11, (1960).

In this study the decay of the continuum of the air afterglow was found to be equal in the whole spectral range used. In the beginning of the airglow NO is not constant. N atoms from the discharge create O atoms by reacting with NO and retard the intensity decay. Later NO remains constant during the afterglow. It is pointed out that the decay curves measured in the nitric oxide and in the Lewis-Rayleigh stage agree with the current theories of

recombination of N_2 and NO by three-body collision. The author also states that if the spectral intensity distribution in the Lewis-Rayleigh afterglow is due to the action of different third bodies as suggested by Reinecke [Z. Physik, 135, 361, (1953)], his opinion should be improved by accepting a two-step reaction. The measurements can be interpreted if the first step is responsible to the rate and the second step to the intensity distribution.

It is concluded that no sign could be found for the Cario-Kaplan processes

$$N(^2P) + N_2(A_O) \rightarrow N(^4S) + N_2(B_{12})$$

$$N(^2D) + N_2(A_O) \rightarrow N(^4S) + N_2(B_6)$$

to be more frequent in the neighborhood of the exciting discharge than that of recombination. The recombination of N atoms could be shown to be severely hindered by transition into the auroral stage; additional collision processes become effective in the excitation of all transitions of the first positive group.

Fornato, D. and A. Gilardini, "Microwave Determinations of Afterglow Temperatures and Electron Collision Frequencies in Nitrogen", Sindal S.P.A., (Italy), Scientific Note No. 1, AFCRC TN-60-149, (1960).

The authors summarize this report by stating that the electron collision probabilities in nitrogen measured by different authors using microwave techniques show large discrepancies. In the present report the method for determining the afterglow electron temperatures from microwave noise measurements is fully described.

The results are shown graphically in Figure 4 of the report. It was found that in the nitrogen afterglow of a d.c. pulsed discharge in a long glass tube the electron temperature is much higher than room temperature. The authors offer as a possible reason for the high temperatures the presence of energetic electrons coming from ionizing metastable collisions. The authors conclude that this continuous source of electrons in the afterglow is also required to explain the observed slow electron density decay.

Chamberlain, J.W. and C. Sagan, "The Origin of Nitrogen Ionization in the Upper Atmosphere", Planetary & Space Sci., 2, 157-164, (1960).

Reference is made to Slipher (1933) who first reported a twilight enhancement of the airglow, the first negative bands of N_2^+ $[B\ {}^2\Sigma_u^+ \rightarrow X\ {}^2\Sigma_g^+]$. The recombination of N_2^+ ions proceeds rapidly through dissociative recombination

$$N_2^+ + e^- \rightarrow N^* + N^{**}$$

where the nitrogen atoms may be in excited terms. According to Bialecke and Dougal (1958) a rate coefficient for the dissociative recombination reaction was given as $\alpha = 7 \times 10^{-7}\ cm^3\ sec^{-1}$.

When there is no longer any ionizing radiation, the mean lifetime of N_2^+ is $\tau \simeq (n_e\ \alpha\ sec)^{-1}$, assuming that $n_e \simeq 10^4$ electrons cm^{-3} which is appropriate to the early evening value of $\tau = 2$ min.

The authors conclude that the symmetry of morning and evening observations make it unlikely that the ionization is produced by sunlight in the E-region. Four principle sources for the solar radiation are considered: the ultraviolet continuum, λ 304A(He II)

and λ 584A (He I) line emissions, and soft X-rays.

According to Rense (1958) the flux in the He II λ304A line is about 15 erg cm^{-2} sec^{-1} (2 x 10^{11} photons cm^{-2} sec^{-1}), while Hinteregger (1959) derived a flux for He II λ304 which is a factor of 10^3 less. In the present paper the authors show that if the flux of the He II λ304A line is as high as 15 erg cm^{-2} sec^{-1}, the observed first negative system intensities can be accounted for and the nitrogen ionization will be localized in the F-region.

Heath, Donald Frederick, "New Data on the Emission Spectrum of Air", U.S. Atomic Energy Comm., LA-2335, 79 pp., (1960).

The purpose of this investigation was to clarify the mechanism by which the first positive group of N_2 bands is weakened in a discharge in air at reasonably high pressure. The work was concerned with the study of the emission features of the air spectrum produced by continuous excitation. The chief constituents in the normal air spectrum are the band systems of N_2, N_2^+, O_2, O_2^+, NO, NO^+, OH, NO_2, CO, CO^+, and atomic spectra of the first few stages of ionization of N, O, Ar, H, and possibly minor constituents such as Na and C. Each of these constituents was observed and investigated over a wide range of pressure (0.01 to 760 mm). Excellent energy level diagrams for the species responsible for the emission spectrum of air are given in the appendix of the report.

With reference to the N_2^+ negative bands it is stated that the bands which belong to the system B $^2\Sigma_u \rightarrow$ X $^2\Sigma_g^+$ lie in the wavelength region 3000 to 5900 A and appear readily in N_2, air, and NO discharges. For discharges in pure nitrogen, the intensity of the negative bands relative to the second positive group reached a maximum between

a pressure of 0.1 and 1.0 mm. There was evidence for the suppression of the negative bands in the presence of even small amounts of O_2 or NO in the N_2 discharges as observed from discharges in 9.7 mm N_2 and 0.3 mm NO or O_2. The negative bands from the v' = O were eight times more intense in a pure N_2 discharge at 10 mm than in a discharge of 9.7 mm N_2 and 0.3 mm NO or O_2 for the same intensity of the second positive group. At atmospheric pressure there were no indications that the negative bands are suppressed, which is contrary to the results of Feast [Proc. Phys. Soc., (London), A 63, 563, (1950)] who observed that the negative bands of N_2 are strengthened by the removal of oxygen from low current, high voltage arcs in nitrogen at atmospheric pressure.

In respect to atomic nitrogen N I the strongest lines were found in the region 8200 to 8700 Å. In general with increasing gas pressure, the intensities of all N I lines decrease relative to the second positive group.

The second spectrum of N (N II) was observed in air and NO but not in N_2 discharges. The easily observed lines were in the region 4600 to 6500 A. Discharges in air gave rise to the second spectrum of N only near atmospheric pressure. The author concludes that the disappearance of the first positive group of N_2 in high pressure air discharges is most probably the result of a resonance transfer of energy from the N_2 molecules in the upper state of this system to unexcited NO molecules. The collision induces the radiationless transition in N_2

$$B\ {}^3\Pi_g \rightarrow X\ {}^1\Sigma_g^+ .$$

Jones, A. Vallance and D. M. Hunten, "Rotational and Vibrational

Intensity Distribution of the First Negative N_2^+ Bands in Sunlit Auroral Rays", Can. J. Phys., 38, 458-476, (1960).

This paper is a report of the spectra of sunlit auroral rays which were obtained from Saskatoon, Canada, during the auroras of 3/4 and 4/5 September 1958. Reference is made to Störmer [Terrest. Mag. Atmos. Elect., 44, 7, (1939)] who obtained spectra of sunlit auroral rays. These rays were at heights between 400 and 650 km and showed the first negative N_2^+ bands to be particularly strong and to exhibit an unusually great development of the vibrational sequences.

In the present investigation the resolution of the spectra was sufficiently high to enable measurement of the relative intensities of the lines of the O-O first negative N_2^+ bands as well as the relative intensities of bands of the $\Delta v = -1$ sequence of this system. The life of the N_2^+ ion is ended by the dissociative recombination process $N_2^+ + e^- \rightarrow N + N$ which according to Faire and Champion [Phys. Rev., 113, 1, (1959)] has a large coefficient of 4.0×10^{-7} cm^3/sec. In the presence of aurora it is stated that the electron density is probably about $n(e) = 5 \times 10^5/cm^3$. Thus the mean lifetime of the N_2^+ ion is only about 50 seconds. A smaller electron density would give a longer life; however, it is unlikely to exceed 200 seconds and may be as short as 5 seconds. A kinetic temperature of about $2000^{\circ}K$ in the 400 to 500-km region was indicated by this investigation.

Klein, Ralph and Erwin M. Horl, "Isotope Exchange Processes in Solid Nitrogen under Electron Bombardment", J. Chem. Phys., 32, 307-308, (1960).

The glow from solid nitrogen when irradiated with electrons is known to involve atomic transitions. Thus ground state ^4S atoms have been observed in irradiated solid nitrogen at $4.2^{o}K$ with electron paramagnetic resonance and ^2D and ^2P atoms have been observed by their emission spectra. The experimental data were measured in terms of G values from the study of the isotope exchange in mixtures of $N^{14}N^{14} - N^{15}N^{15}$. The G value for the exchange process at $4.2^{o}K$ was found to be about 0.2.

The authors state that atom recombination may lead to isotope exchange. Processes such as

$$N(^2D) + N_2(X\ ^1\Sigma_g^+) \rightarrow N_2 + N$$

may occur. Excited molecule-molecule, excited ion-molecule, or ion-excited molecule reactions may also lead to exchange.

Krasovskii, V.I., "Results of Scientific Investigations Made from Soviet Sputniks and Cosmic Rockets", ARS Journal, 30, 27-33, (1960).

Before the launching of the first Soviet sputnik the upper atmosphere beginning with the 200-km level was thought to be isothermal and to have a temperature of less than $1000^{o}K$; consequently, the scale height was thought to be small. However by deceleration of the sputniks, it was found that at a height of 220 km the density of the atmosphere was equal to 2.5×10^{-13} g cm^{-3}. This exceeded what had been expected and the result essentially changed the conceptions of density and temperature of the upper atmosphere heretofore accepted.

By changing the period of revolution of sputniks around the earth and by changing the position of the perigee, it was found that at the 220-km level the density of the atmosphere was greater by day than by night and greater in the polar than in the equatorial regions. As a result of a sodium cloud experiment it was estimated that the scale height is 70 km at the 430-km level.

The third Soviet sputnik carried a spectrometer for determining the nature of the atmospheric ions with a mass number of 6 up to 50 units. The ion of nitric oxide (NO) was found to be the most frequent up to the height of 250 km. The existence of this ion up to this height does not mean that it forms as a result of ionization of the neutral molecule of NO. As was shown by a number of theoretical and laboratory investigations, the ionized molecules of NO appear in the upper layers of the atmosphere as a result of the reaction of any oxygen ion with a neutral molecule of nitrogen or in the reaction of the oxygen atom with an ionized molecule of nitrogen.

$$N_2^+ + O^+ \rightarrow NO^+ + N$$

$$N_2^+ + O \rightarrow NO^+ + N$$

The nitrogen ions found show that nitrogen molecules are present at altitudes up to 250 km. However, exploration with the help of the third sputnik revealed that there are only atomic ions of oxygen and nitrogen higher than 250 km; the ions of atomic oxygen are dominant, whereas the ions of atomic nitrogen constitute only several percent of the oxygen ions. This is evidence that the upper atmosphere above 250 km has an atomic structure.

Lytle, E.A. and D.M. Hunten, "Dawn Enhancement of Auroral

N_2^+ Emission", Can. J. Phys., 38, 477-487, (1960).

During this investigation the O-O band at 3914 A was observed once per minute with a scanning spectrometer as sunlight illuminated the upper atmosphere on the morning of 5 September 1958. It seemed reasonable to assume that the density of the N_2^+ ions was constant during this time, and that the observed rise of intensity was due to resonance scattering of sunlight. The ions were found to be distributed between 180 and 320 km with peak intensity at 250 km. At the latter height the density was 12×10^4 ions/ cm^3, nd there was some evidence for another layer at 120 km. These values were deduced from a brightness

$$4\pi B = 62 \text{ k R}$$

for the dawn enhancement observed at a zenith angle of 55°.

Mironov, A.V., V.S. Prokudina, and N.N. Skefov, "The Low-Latitude Aurora of January 21-22, 1957", Bulletin (Izvestiya) Academy Sci. USSR, Geophysics Series, December 1958, English Edition Translated and Published by the Ann. Geophys. Union of the Natl. Acad. Sci. - Natl. Research Council, pp. 885-886, January 1960.

A strong magnetic storm on 21 January 1957 was followed by an intense aurora during the night of 21-22 January. The auroral spectrum was photographed at the Zvenigorod station of the Institute for Physics of the Atmosphere of the USSR Academy of Sciences near Moscow.

The lines of atomic oxygen, nitrogen, and hydrogen and molecular nitrogen were identified in the spectra. Emission lines

of neutral atomic nitrogen occur at λλ 6482, 6468 and 6441 A. The clear first positive bands of N_2 are (6.3), (7.4) and (9.6). A first negative N_2^+ band is also present. This was at (0.2), λ 4709 A.

Ogawa, M. and Y. Tanaka, "New Emission Bands of Forbidden Systems of Nitrogen in the Vacuum Ultraviolet Region", J. Chem. Phys., 32, 754-758, (1960).

Using a 2-meter vacuum spectrograph and an ordinary transformer discharge through mixtures of N_2 with argon and xenon, the authors observed two new systems of N_2 emission bands in the region between 1550 and 2250 A. From vibration analysis, the bands which were excited in the mixture of N_2 and A are due to the transition $(a' \, ^1\Sigma_u^- \rightarrow X \, ^1\Sigma_g^+)$, and the bands which were excited in the mixture of N_2 and Xe are due to the transition $(^3\Sigma_u^- \rightarrow X \, ^1\Sigma_g^+)$.

The authors state that their present results are in good agreement with those of Wilkinson and Mulliken [J. Chem. Phys., 31, 674, (1959)] who made observations on the same systems of bands in absorption.

Verbeke, G.J. and C.A. Winkler, "The Reactions of Active Nitrogen With Nitric Oxide and Nitrogen Dioxide", J. Phys. Chem., 64, 319-323, (1960).

The reactions of active nitrogen with nitric oxide and nitrogen dioxide were studied over a range of reactant flow rates. The experimental procedure is fully described. It is pointed out that the most striking observation of the present study was that nitric

oxide was destroyed by active nitrogen in significantly larger amounts than hydrogen cyanide was formed from ethylene. It was concluded that nitric oxide (NO) reacted with more than one reactive species in active nitrogen. This implied that the measurement of atomic nitrogen concentration from the extent of the NO reaction might be unsatisfactory. The reaction of active nitrogen with NO_2 was observed to yield considerable N_2O. This did not occur with the NO reaction.

In the following equations the heats of reaction are included. These were calculated from the heats of formation from Circular 500, National Bureau of Standards, Washington, 1952.

$$N + NO \rightarrow N_2 + O + 75 \text{ kcal}$$

$$N(^4S) + NO(^2\Pi) \rightarrow N_2O(^1\Sigma) + 114.5 \text{ kcal}$$

$$N + NO_2 \rightarrow N_2O + O + 42 \text{ kcal}$$

$$N + NO_2 \rightarrow N_2 + O_2 + 122 \text{ kcal}$$

$$NO_2 + O \rightarrow NO + O_2 + 47 \text{ kcal}$$

$$NO_2 + N \rightarrow N_2 + 2\,O + 4 \text{ kcal}$$

Young, R. A. and K. C. Clark, "Vibrational Distribution in Late Nitrogen Afterglows", J. Chem. Phys., 32, 604-606, (1960).

This is a report of an investigation of the late portion of nitrogen afterglows at a pressure of 1 mm Hg. The afterglows in active nitrogen consist chiefly of the first positive bands of N_2

($B\ ^3\Pi \rightarrow A\ ^3\Sigma$) with enhancement of those from vibrational levels near v' = 11 and 6. The equipment is fully described. The nitrogen was prepared from sodium azide and the afterglow observed in a spherical 12-liter bulb. This was studied spectroscopically. It is concluded that a common excitation mechanism for all levels is required. It is pointed out that the excitation mechanism cannot depend upon metastable particles formed in the initial discharge or generated during the decay. Figure 1 in the paper shows a representative time-resolved spectrum of the first positive bands in N_2 afterglow at 1 mm Hg pressure. The band identifications are clearly indicated. Figure 2 is a comparison of early and late nitrogen spectra at fixed delay times of 2 and 140 sec. There is a striking similarity of intensity distributions.

Zinman, Walter G., "Recent Advances in Chemical Kinetics of Homogeneous Reactions in Dissociated Air", ARS Jour., 30, 233-238, (1960).

Three-body recombination reactions are considered for: iodine atom recombination, oxygen atom recombination, and nitrogen atom recombination. The author states that k_r for nitrogen atoms with molecular nitrogen as a third body has a value of 5.7 ($\pm$0.8) x 10^{15} cm^6 per gm-mole^2 sec between 195 and 450°K. With argon as a third body this coefficient is 2.8 ($\pm$0.3) x 10^{15} cc^2 per mole^2 sec at 297°K. The reference cited for the first value is Herron, Franklin, Bradt and Dibeler (1959); the paper by Harteck, Reeves, and Mannella (1958) provided the second value. It is pointed out that the value of the recombination coefficient of nitrogen atoms at 297°K with argon as a third body is the same as the corresponding recombination coefficient for iodine atoms.

3. AUTHOR INDEX

4. SUBJECT INDEX

GEOPHYSICAL RESEARCH PAPERS

No. 1. Isotropic and Non-Isotropic Turbulence in the Atmospheric Surface Layer, *Heinz Lettau, Dec 1949.*

No. 2. Effective Radiation Temperatures of the Ozonosphere over New Mexico, *A. L. Adel, Dec 1949.*

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No. 5. Investigation of Stratosphere Winds and Temperatures From Acoustical Propagation Studies, *Albert P. Crary, Jun 1950.*

No. 6. Air-Coupled Flexural Waves in Floating Ice, *F. Press, M. Ewing, A. P. Crary, S. Katz and J. Oliver, Nov 1950.*

No. 7. Proceedings of the Conference on Ionospheric Research (June 1949), *edited by Bradford B. Underhill and Ralph J. Donaldson, Jr., Dec 1950.*

No. 8. Proceedings of the Colloquium on Mesospheric Physics, *edited by N. C. Gerson, Jul 1951.*

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No. 10. The Measurement of Stratospheric Density Distribution with the Searchlight Technique, *L. Elterman, Dec 1951.*

No. 11. Proceedings of the Conference on Ionospheric Physics (July 1950) Part A, *edited by N. C. Gerson and Ralph J. Donaldson, Jr., Apr 1952.*

No. 12. Proceedings of the Conference on Ionospheric Physics (July 1950) Part B, *edited by Ludwig Katz and N. C. Gerson, Apr 1952.*

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